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**Preparing catalyst for olefin polymerization**

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NON-CONVENTION

AUSTRALIA

Patents Act 1990

650808

REQUEST FOR A STANDARD PATENT

AND NOTICE OF ENTITLEMENT

The Applicant identified below requests the grant of a patent to the nominated person identified below for an invention described in the accompanying standard complete patent specification.

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[54]Invention Title:

PREPARING CATALYST FOR OLEFIN POLYMERIZATION

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Applicant states the following:

The nominated person is the assignee of the actual inventor(s)

The nominated person is not an opponent or eligible person described in Section 33-36 of the Act.

21 January 1993

Phillips Petroleum Company

By PHILLIPS ORMONDE & FITZPATRICK

Patent Attorneys

By

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Our Ref : 316620

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- (54) Title  
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- (57) Claim

1. A process to prepare a catalyst system comprising combining a metal source, a pyrrole-containing compound and a metal alkyl in a mutual solvent without a preliminary reaction step between the metal source and the pyrrole-containing compound in the presence of an electron donor solvent.

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COMPLETE SPECIFICATION  
(ORIGINAL)

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Invention Title:

PREPARING CATALYST FOR OLEFIN POLYMERIZATION

Our Ref : 316620  
POF Code: 1422/50647

The following statement is a full description of this invention, including the best method of performing it known to applicant(s):



This invention relates to chromium catalysts or cocatalysts to trimerize, oligomerize and/or polymerize olefins. This invention also relates to a process to trimerize, oligomerize and/or polymerize olefins.

Supported chromium oxide catalysts have been a dominant factor in the production of olefin polymers, such as polyethylene or copolymers of ethylene and hexene. These catalysts can be used in a variety of polymerization processes. However, most known chromium compounds must be supported to be catalytically active. Furthermore, most supported chromium compounds are useful only for olefin polymerization. If an olefin copolymer is desired, the polymerization process becomes more complex in that two different monomers must be fed to the polymerization reactor.

Olefin trimerization and oligomerization catalysts are also known in the art, but usually lack selectivity to a desired product and also have a low product yield. However, olefin trimerization and/or oligomerization, if done efficiently, is a process to provide useful olefins. These olefinic products can be further trimerized, oligomerized and/or, optionally, incorporated into a polymerization process.

In accordance with our Patent Application 60296/90 filed 8 August 1990 there is described a chromium-containing compound having the formula:

$\text{Cr}_5(\text{C}_6\text{H}_5\text{N})_{10}(\text{C}_6\text{H}_5\text{O})_4$ ;  $[\text{Cr}(\text{C}_6\text{H}_5\text{N})_4][\text{Na}]_2 \cdot 2(\text{OC}_6\text{H}_5)$ ;  
[ $\text{Cr}(\text{C}_6\text{H}_5\text{N})_5(\text{OC}_6\text{H}_5)$ ][ $\text{Na}$ ] $_4 \cdot 4(\text{OC}_6\text{H}_5)$ ; or  
 $\text{Cr}(\text{NC}_6\text{H}_5)_3\text{Cl}(\text{O}_2\text{C}_2\text{H}_5(\text{CH}_3)_2)_3\text{Na}$ .

In accordance with an aspect of the above  
5 application, such novel chromium-containing compounds  
are prepared from a reaction mixture comprising a  
chromium salt, a metal amide, and any electron pair  
donor solvent, such as, for example, an ether. The  
catalyst systems can be used, either supported or  
10 unsupported, to trimerize and/or polymerize olefins.

The chromium salt can be one or more organic  
or inorganic chromium salts, wherein the chromium  
oxidation state is from 0 to 6. As used in this  
disclosure, chromium metal is included in this  
15 definition of a chromium salt. Generally, the chromium  
salt will have a formula of  $\text{CrX}_n$ , wherein X can be the  
same or different and can be any organic or inorganic  
radical, and n is an integer from 1 to 6. Exemplary  
organic radicals can have from about 1 to about 20  
20 carbon atoms per radical, and are selected from the  
group consisting of alkyl, alkoxy, ester, ketone,  
and/or amido radicals. The organic radicals can be  
straight-chained or branched, cyclic or acyclic,  
aromatic or aliphatic, and can be made of mixed  
25 aliphatic, aromatic, and/or cycloaliphatic groups.  
Exemplary inorganic radicals include, but are not  
limited to halides, sulfates, and/or oxides.

Preferably, the chromium salt is a halide,  
such as, for example chromous fluoride, chromic  
30 fluoride, chromous chloride, chromic chloride, chromous  
bromide, chromic bromide, chromous iodide, chromic  
iodide, and mixtures thereof. Most preferably, the  
chromium salt is a chloride, such as, for example  
chromous chloride and/or chromic chloride, due to  
35 simple separation of the reaction by-products such as,  
for example, sodium chloride, as well as relatively low  
cost.

The metal amide can be any metal amide that will react with a chromium salt to form a chromium-amido complex. Broadly, the metal amide can be any heteroleptic or homoleptic metal complex or salt, wherein the amide radical can be any nitrogen-containing organic radical. The metal amide can be either affirmatively added to the reaction, or generated in-situ. Generally, the metal amide will have from about 1 to about 20 carbon atoms.

Exemplary preferred metal amides include, but are not limited to, lithium dimethylamide, lithium diethylamide, lithium diisopropylamide, lithium dicyclohexylamide, sodium bis(trimethylsilyl)amide, sodium indolide, alkali metal and alkaline earth metal pyrrolides, and mixtures of two or more thereof. Most preferred are the above metal pyrrolides such as lithium pyrrolide, sodium pyrrolide, potassium pyrrolide, and cesium pyrrolide, because of high reactivity and activity with the other reactants. Examples of substituted pyrrolides include, but are not limited to sodium 2,5-dimethyl pyrrolide and/or 3,4-dimethyl pyrrolide. When the metal amide is a pyrrolide ligand, the resultant chromium compound is a chromium pyrrolide.

In accordance with a first aspect of the present invention pyrrole itself (hydrogen pyrrolide) or a substituted pyrrole is recognized as a suitable pyrrolide. Pyrrole is a preferred hydrogen pyrrolide. ~~Substituted pyrroles are illustrated below.~~

The ether in the reaction mixture can be one or more ether compounds to effect a reaction between the chromium salt and the metal amide. While not wishing to be bound by theory, it is believed that the ether can be a reaction solvent, as well as a possible reactant. The ether can be any aliphatic and/or aromatic compound containing an R-O-R functionality, wherein the R groups can be the same or different, but ~~preferably is not hydrogen. Preferred ethers are~~



Substituted pyrroles are illustrated below. Said first aspect of the invention provides a process to prepare a catalyst system comprising reacting a mixture of:

- (a) a metal salt;
- (b) pyrrole or a substituted pyrrole; and
- (c) an electron pair donor solvent and reacting the resulting reaction product with a metal alkyl; and, if desired, reacting the resulting reaction product with an unsaturated hydrocarbon.

The ether in the reaction mixture can be one or more ether compounds to effect a reaction between the chromium salt and the metal amide. While not wishing to be bound by theory, it is believed that the ether can be a reaction solvent, as well as a possible reactant. The ether can be any aliphatic and/or aromatic compound containing an R-O-R functionality, wherein the R groups can be the same or different, but preferably is not hydrogen. Preferred ethers are



aliphatic ethers, for safety reasons in that aromatic ethers are human toxins. Furthermore, the preferred ethers are those which facilitate a reaction between a chromium halide and a Group IA or Group IIA metal pyrrolide, and also can be easily removed from the reaction mixture. Exemplary compounds include, but are not limited to, tetrahydrofuran, dioxane, diethylether, dimethoxyethane (glyme), diglyme, triglyme, and mixtures of two or more thereof. Most preferably, the ether is selected from the group consisting of tetrahydrofuran, derivatives of tetrahydrofuran, dimethoxyethane, derivatives of dimethoxyethane, and mixtures thereof, for the reasons given above, as well as the reason that the preferred salt of an amine is soluble in these ethers.

The three reactants can be combined in any manner under conditions suitable to form a solution comprising one or more of the inventive chromium compounds. The reaction preferably occurs in the absence of oxygen and moisture and therefore under an inert atmosphere, such as, for example nitrogen and/or argon. The reaction pressure can be any pressure sufficient to maintain the reactants in a liquid state. Generally, pressure within the range of from about atmospheric pressure to about three atmospheres are acceptable. For ease of operation atmospheric pressure is generally employed.

The precipitated inventive chromium compounds can be recovered by any method known in the art. The simplest procedure to remove the precipitated chromium compounds is by filtration.

~~In accordance with a second aspect of the present invention, the metal pyrrolides useful as catalysts or cocatalysts can also be prepared from salts of metals other than chromium. Exemplary metals include nickel, cobalt, iron, molybdenum, and copper. As with the chromium salt, the metal oxidation state of~~



In accordance with a second aspect of the present invention, the metal pyrrolides useful as catalysts or cocatalysts can also be prepared from salts of metals other than chromium. Said second aspect of the invention provides a process to prepare a catalyst system comprising reacting a mixture of:

- (a) a salt of a metal other than chromium;
- (b) a metal amide; and
- (c) an electron pair donor solvent; and reacting the resulting reaction product with a metal alkyl; and if desired, reacting the resulting reaction product with an unsaturated hydrocarbon. Exemplary metals included nickel, cobalt, iron, molybdenum, and copper. As with the chromium salt, the metal oxidation state of



the metal can be any oxidation state, including the elemental, or metallic, state. These novel metal pyrrolides can be prepared in a manner similar to the previously described chromium pyrrolides.

5       The chromium or other metal compounds prepared by the above process can be used, either as a supported and/or unsupported catalyst system, for olefin trimerization, oligomerization and/or polymerization. A supported chromium catalyst system  
10 can be prepared with any support useful to support a chromium catalyst. Exemplary catalyst supports include, but are not limited to, zeolites, inorganic oxides, either alone or in combination, phosphated inorganic oxides, and mixtures thereof. Particularly  
15 preferred are supports selected from the group consisting of silica, silica-alumina, alumina, fluorided alumina, sited alumina, thoria, aluminophosphate, aluminum phosphate, phosphated silica, phosphated alumina, silica-titania,  
20 coprecipitated silica/titania, fluorided/sited alumina, and mixtures, thereof, being presently preferred, as well as any one or more of these supports which can contain chromium. The presently most preferred catalyst support, because of the greatest  
25 trimerization activity, is aluminophosphate, as disclosed in U.S. Patent 4,364,855 (1982).

      The amount of chromium pyrrolide compound per gram of support can be expressed in different, yet equivalent terms, such as, for example, moles of  
30 chromium per gram of support. Usually, less than about  $8.6 \times 10^{-3}$  moles of chromium per gram of support is sufficient. Preferably, about  $1.7 \times 10^{-6}$  to about  $1.7 \times 10^{-5}$  to  $8.6 \times 10^{-4}$  moles of chromium per gram of support are used, for reasons given above.

35       After the support is added and thoroughly combined with the chromium pyrrolide, it can be collected by filtration, vacuum dried, then an

activating compound, usually as a solution of one or more Lewis acids and/or metal alkyls, preferably in hydrocarbon compound solvent, is added to the support/chromium pyrrolide mixture. An active, supported catalyst system then can be collected by filtration. As used in this disclosure, a Lewis acid is defined as any compound that is an electron acceptor. Preferably, the activating compound is a compound that can be considered both a Lewis acid and a metal alkyl. As more broadly described in the present application, the activating compound can have any number of carbon atoms. However, due to commercial availability and ease of use, the activating compound will usually comprise less than about 70 carbon atoms per metal alkyl molecule and preferably less than about 20 carbon atoms per molecule. Preferred activating compounds which are both a metal alkyl and a Lewis acid include, but are not limited to, alkylaluminum compounds, alkylboron compounds, alkylmagnesium, alkylzinc, and/or alkyl lithium compounds. Exemplary metal alkyls include, but are not limited to, n-butyllithium, s-butyllithium, t-butyllithium, diethylmagnesium, dibutylmagnesium, diethylzinc, triethylaluminum, trimethylaluminum, triisobutylaluminum, and mixtures thereof. Most preferably, activating compounds are selected from the group consisting of non-hydrolyzed, i.e., not pre-contacted with water, alkylaluminum compounds, derivatives of alkylaluminum compounds, halogenated alkylaluminum compounds, and mixtures thereof for improved product selectivity, as well as improved catalyst system reactivity, activity, and/or productivity. Exemplary compounds include, but are not limited to, triethylaluminum, tripropylaluminum, tributylaluminum, diethylaluminum chloride, diethylaluminum bromide, diethylaluminum ethoxide, ethylaluminum sesquichloride, and mixtures thereof for



best catalyst system activity and product selectivity. The most preferred alkylaluminum compound is triethylaluminum, for best results in catalyst system activity and product selectivity.

5 Any amount of activating compound, such as a metal alkyl and/or a Lewis acid, is sufficient to activate and/or react with the chromium pyrrolide catalyst. Usually about 200 grams of activating  
10 compound, i.e., metal alkyl and/or a Lewis acid, per gram of chromium can be used. Preferably, about 1 to about 100 grams of activating compound, such as a metal alkyl and/or a Lewis acid, per gram of chromium pyrrolide, and most preferably about 5 to about 30  
15 grams of activating compound, such as a metal alkyl and/or a Lewis acid, per gram of chromium pyrrolide are used, for best catalyst activity. However, the amount of activating compound, such as a metal alkyl and/or a Lewis acid employed can vary with the catalyst support  
20 used. For example, if the support is silica and/or alumina, too much activating compound, such as a metal alkyl and/or a Lewis acid can decrease catalyst activity. However, a similar amount of activating compound, such as a metal alkyl and/or a Lewis acid, used with an aluminophosphate support does not always  
25 significantly decrease catalyst activity.

As more broadly described herein, the hydrocarbon compound used as a solvent can be any combination of one or more aromatic or aliphatic  
30 unsaturated hydrocarbon compounds. While not wishing to be bound by theory, it is believed that an unsaturated hydrocarbon compound acts as more than a solvent, and can be a reactant and/or a stabilizing component during and/or subsequent to formation of an inventive catalyst system. Exemplary unsaturated  
35 hydrocarbon compounds, such as, for example, a solvent, can be any unsaturated hydrocarbon compound that can dissolve the activating compound, i.e., wherein the

activating compound can be Lewis acid and/or metal alkyl. In accordance with a third aspect of the present invention in addition to the aromatic compounds having from about 6 to about 50 carbon atoms per molecule as a solvent as described in our above application there can be used unsaturated aliphatic hydrocarbons comprising less than about 20 carbon atoms per molecule. Said third aspect of the present invention provides a process to prepare a catalyst system comprising reacting a mixture of:

- (a) a metal salt;
- (b) a metal amide; and
- (c) an electron pair donor solvent and reacting the resulting reaction product with a metal alkyl; and reacting the resulting reaction product with an unsaturated aliphatic hydrocarbon comprising less than 20 carbon atoms per molecule. Specific exemplary unsaturated aliphatic compounds include

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~~activating compound can be Lewis acid and/or metal~~

alkyl. In accordance, a third aspect of the present invention in addition to the aromatic compounds having from about 6 to about 50 carbon atoms per molecule as a solvent as described in our above application there can be used unsaturated aliphatic hydrocarbons comprising less than about 20 carbon atoms per molecule. Specific

~~exemplary unsaturated aliphatic compounds include~~

ethylene, 1-hexene, 1,3-butadiene, and mixtures

thereof. The most preferred unsaturated aliphatic hydrocarbon compound is ethylene because of elimination of catalyst system preparation steps and ethylene can be a trimerization and/or oligomerization reactant.

Specific exemplary unsaturated aromatic hydrocarbon compounds include, but are not limited to, toluene, benzene, xylene, mesitylene, hexamethylbenzene, and mixtures thereof. As described in our above

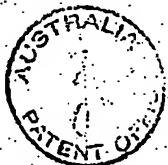
application, the most preferred unsaturated aromatic hydrocarbon compound solvent is toluene, for ease of removal and minimal interference with the resultant catalyst system.

The unsaturated hydrocarbon compound can be present either during the initial contacting of a chromium pyrrolide and activating compound, i.e., prior

to introduction into a trimerization, oligomerization and/or polymerization reactor, or the unsaturated hydrocarbon compound can be introduced directly into the reactor. As stated above, one or more of the olefin reactants can be considered the unsaturated

hydrocarbon. Preferably, the unsaturated hydrocarbon is present during the initial contacting of a chromium pyrrolide and activating compound in order to stabilize the resultant catalyst system. In the absence of an unsaturated hydrocarbon, the resultant catalyst system can deactivate and lose activity over a period of time.

While any amount of unsaturated hydrocarbon compound can be used, too much or too little can



adversely affect catalyst system activity. Therefore, preferably, the resultant catalyst system is stripped of any excess unsaturated aromatic hydrocarbon.

Stripping of excess unsaturated aromatic hydrocarbon can be accomplished by any method known in the art, such as, for example, solvent removal methods.

Exemplary removal methods include, but are not limited to, filtration, vacuum drying, drying under an inert atmosphere, and combinations thereof. While not wishing to be bound by theory, it is believed that the remaining unsaturated hydrocarbon can stabilize the resultant catalyst system. If no unsaturated hydrocarbon is present, it is believed that the catalyst system can lose activity.

An alternative, and then preferred, method in accordance with the above application to produce a supported catalyst system is to combine one or more solid, inventive chromium pyrrolide compounds with an unsaturated hydrocarbon solvent, as more broadly disclosed herein, so as to include, for example, toluene and/or ethylene, and an activating compound, as disclosed earlier, such as a metal alkyl and/or a Lewis acid, such as, for example, triethylaluminum.

In accordance with a fourth aspect of the present invention, a catalyst system can be prepared by combining a metal source, a pyrrole-containing compound, and a metal alkyl and, preferably an unsaturated hydrocarbon compound, in a mutual solvent without a preliminary reaction step using an electron donor solvent (for reaction between the metal source and the pyrrole-containing compound as described

~~above). The optional unsaturated hydrocarbon, for example toluene, can serve as the mutual solvent. In the absence of such an unsaturated hydrocarbon serving as the mutual solvent, there can be used, for example,~~



above). Said fourth aspect of the invention provides a process to prepare a catalyst system comprising combining a metal source, a pyrrole-containing compound and a metal alkyl in a mutual solvent without a preliminary reaction  
5 step between the metal source and the pyrrole-containing compound in the presence of an electron donor solvent. The optional unsaturated hydrocarbon, for example toluene, can serve as the mutual solvent. In the absence of such  
10 an unsaturated hydrocarbon serving as the mutual solvent, there can be used, for example,

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cyclohexane. These catalyst systems can further comprise a catalyst support. Preferably the metal source is a chromium source but can be any of the other metals as described above.

5 The chromium source, similar to the earlier discussed chromium salt, can be one or more organic or inorganic chromium compounds, wherein the chromium oxidation state is from 0 to 6. As used in this disclosure, chromium metal is included in this  
10 definition of a chromium salt. Generally, the chromium source will have a formula of  $\text{CrX}_n$ , wherein X can be the same or different and can be any organic or inorganic radical, and n is an integer from 1 to 6. Exemplary  
15 organic radicals can have from about 1 to about 20 carbon atoms per radical, and are selected from the group consisting of alkyl, alkoxy, ester, ketone, and/or amido radicals. The organic radicals can be straight-chained or branched, cyclic or acyclic,  
20 aromatic or aliphatic, can be made of mixed aliphatic, aromatic, and/or cycloaliphatic groups. Exemplary inorganic radicals include, but are not limited to halides, sulfates, and/or oxides.

Preferably, the chromium source is a chromium(II)- and/or chromium(III)-containing compound  
25 which can yield a catalyst system with improved trimerization activity. Most preferably, the chromium source is a chromium(III) compound because of ease of use, availability, and enhanced catalyst system activity. Exemplary chromium(III) compounds include,  
30 but are not limited to, chromium carboxylates, chromium naphthenates, chromium halides, chromium pyrrolides, and/or chromium dionates. Specific exemplary chromium(III) compounds include, but are not limited to, chromium(III) 2,2,6,6-tetramethylheptanedionate  
35  $[\text{Cr}(\text{TMHD})_3]$ , chromium(III) 2-ethylhexanoate  $[\text{Cr}(\text{EH})_3]$ , chromium(III) naphthenate  $[\text{Cr}(\text{Np})_3]$ , chromium(III)

chloride, chromium (III)-tris(2-ethylhexanoate),  
chromic bromide, chromic chloride, chromic fluoride,  
chromium (III) oxy-2-ethylhexanoate, chromium (III)  
dichloroethylhexanoate, chromium (III) acetylacetonate,  
5 chromium (III) acetate, chromium (III) butyrate,  
chromium (III) neopentanoate, chromium (III) laurate,  
chromium (III) stearate, chromium (III) pyrrolide(s),  
and/or chromium (III) oxalate.

Specific exemplary chromium (II) compounds  
10 include, but are not limited to, chromous fluoride,  
chromous chloride, chromous bromide, chromous iodide  
chromium (II) bis(2-ethylhexanoate), chromium (II)  
acetate, chromium (II) butyrate, chromium (II) neopent-  
anoate, chromium (II) laurate, chromium (II) stearate,  
15 chromium (II) pyrrolides, and/or chromium (II) oxalate.

The pyrrole-containing compound can be any  
pyrrole-containing compound that will react with a  
chromium salt to form a chromium pyrrolide complex. As  
used in this disclosure, the term "pyrrole-containing  
20 compound" refers to hydrogen pyrrolide, i.e., pyrrole,  
(C<sub>4</sub>H<sub>5</sub>N), derivatives of hydrogen pyrrolide, as well as  
metal pyrrolide complexes. A "pyrrolide" (or a  
"pyrrole" as referred to in the first aspect of the  
invention) can be any compound comprising a 5-membered,  
25 nitrogen-containing heterocycle, such as, for example,  
pyrrole, derivatives of pyrrole, and mixtures thereof.  
Broadly, the pyrrole-containing compound can be pyrrole  
and/or any heteroleptic or homoleptic metal complex or  
salt, containing a pyrrolide radical, or ligand. The  
30 pyrrole-containing compound can be either affirmatively  
added to the reaction, or generated in-situ.

Generally, the pyrrole-containing compound will have  
from about 1 to about 20 carbon atoms per molecule.  
Exemplary pyrrolides (or pyrroles) include hydrogen  
35 pyrrolide (pyrrole), derivatives of pyrrole,  
substituted pyrrolides (or pyrroles), lithium  
pyrrolide, sodium pyrrolide, potassium pyrrolide,

cesium pyrrolide, and/or the salts of substituted pyrrolides, because of high reactivity and activity with the other reactants. Examples of substituted pyrrolides (or pyrroles) include, but are not limited to pyrrole-2-carboxylic acid, 2-acetylpyrrole, pyrrole-2-carboxaldehyde, tetrahydroindole, 2,5-dimethylpyrrole, 2,4-dimethyl-3-ethylpyrrole, 3-acetyl-2,4-dimethylpyrrole, ethyl-2,4-dimethyl-5-(ethoxycarbonyl)-3-pyrrole-propionate, ethyl-3,5-dimethyl-2-pyrrole-carboxylate. When the pyrrole-containing compound contains chromium, the resultant chromium compound can be called a chromium pyrrolide.

The most preferred pyrrole-containing compounds used in a trimerization catalyst system are selected from the group consisting of hydrogen pyrrolide, i.e., pyrrole ( $C_4H_5N$ ) and/or 2,5-dimethylpyrrole. While all pyrrole-containing compounds can produce catalysts with high activity and productivity, use of pyrrole and/or 2,5-dimethylpyrrole can produce a catalyst system with enhanced activity and selectivity to a desired trimerized product, such as, for example, the trimerization of ethylene to 1-hexene, as well as decreased polymer production.

The metal alkyl, also referred to earlier as an activating compound, can be any heteroleptic or homoleptic metal alkyl compound. One or more metal alkyls can be used. The ligand(s) on the metal can be aliphatic and/or aromatic. Preferably, the ligand(s) are any saturated or unsaturated aliphatic radical. The metal alkyl can have any number of carbon atoms. However, due to commercial availability and ease of use, the metal alkyl will usually comprise less than about 70 carbon atoms per metal alkyl molecule and preferably less than about 20 carbon atoms per molecule. Preferred metal alkyls include, but are not limited to, alkylaluminum compounds, alkylboron compounds, alkylmagnesium compounds, alkylzinc



compounds and/or alkylolithium compounds. Exemplary metal alkyls include, but are not limited to, n-butyllithium, s-butyllithium, t-butyllithium, diethylmagnesium, diethylzinc, triethylaluminum, trimethylaluminum, triisobutylaluminum, and mixtures thereof.

Most preferably, activating compounds are selected from the group consisting of non-hydrolyzed, i.e., not pre-contacted with water, alkylaluminum compounds, derivatives of alkylaluminum compounds, halogenated alkylaluminum compounds, and mixtures thereof for improved product selectivity, as well as improved catalyst system reactivity, activity, and/or productivity. Exemplary compounds include, but are not limited to, triethylaluminum, tripropylaluminum, tributylaluminum, diethylaluminum chloride, diethylaluminum bromide, diethylaluminum ethoxide, ethylaluminum sesquichloride, and mixtures thereof for best catalyst system activity and product selectivity. The most preferred alkylaluminum compound is triethylaluminum, for best results in catalyst system activity and product selectivity, as well as commercial availability.

When a trimerization catalyst system is the desired product, the activating compound must be at least one non-hydrolyzed alkylaluminum compound, expressed by the general formulae  $AlR_3$ ,  $AlR_2X$ ,  $AlRX_2$ ,  $AlR_2OR$ ,  $AlRXOR$ , and/or  $Al_2R_3X_3$ , wherein R is an alkyl group and X is a halogen atom. Exemplary compounds include, but are not limited to, triethylaluminum, tripropylaluminum, tributylaluminum, diethylaluminumchloride, diethylaluminumbromide, diethylaluminummethoxide, diethylaluminum phenoxide, ethylaluminummethoxychloride, and/or ethylaluminum sesquichloride. Preferably, the activating compound for a trimerization catalyst system is a trialkylaluminum compound,  $AlR_3$ , for reasons given

above. The most preferred trialkylaluminum compound is triethylaluminum, for reasons given above.

Formation of stable and active catalyst systems can take place in the presence of an unsaturated hydrocarbon. As discussed in the previous embodiment, an unsaturated hydrocarbon can be present either during the initial contacting of a chromium source, a pyrrole-containing compound and a metal alkyl, or can be introduced directly into a trimerization, oligomerization and/or polymerization reactor. Furthermore, one or more of the olefin reactants can be considered the unsaturated hydrocarbon.

Any unsaturated aromatic or aliphatic hydrocarbon can be used. Preferably, an unsaturated hydrocarbon initially is present in the reaction mixture and most preferably, an aromatic hydrocarbon and/or ethylene initially is present to produce a highly active catalyst in terms of activity and selectivity, as well as a stable catalyst system. The unsaturated hydrocarbon can have any number of carbon atoms per molecule. Usually, the unsaturated hydrocarbon will comprise less than about 70 carbon atoms per molecule, preferably less than about 20 carbon atoms per molecule, due to commercial availability and ease of use.

The unsaturated hydrocarbon can be a gas, liquid, or solid. Preferably, to effect thorough contacting and mixing of the chromium salt, pyrrole-containing compound, and metal alkyl, the unsaturated hydrocarbon will be in a liquid and/or dissolved state. Exemplary unsaturated aliphatic hydrocarbons include, but are not limited to, ethylene, 1-hexene, 1,3-butadiene, and mixtures thereof. The most preferred unsaturated aliphatic hydrocarbon is ethylene, since ethylene can be a reactant during trimerization, oligomerization, and/or polymerization. Exemplary unsaturated aromatic hydrocarbons include, but are not

limited to, toluene, benzene, xylene, mesitylene, hexamethylbenzene, and mixtures thereof. Unsaturated hydrocarbons are preferred in order to improve catalyst system stability, as well as improve catalyst system activity. The most preferred unsaturated aromatic hydrocarbon is toluene, for best resultant catalyst system stability and activity.

If an unsaturated aromatic hydrocarbon is added prior to introduction of the chromium compound(s) to a trimerization, oligomerization and/or polymerization reactor, removal of, or stripping, the unsaturated aromatic hydrocarbon prior to introduction of the chromium compound(s) into a reactor can improve catalyst system activity and/or product selectivity.

Removal of the unsaturated aromatic hydrocarbon can be done in any manner known in the art, such as, for example, flashing or evaporation. The resultant product is a concentrated, or saturated, solution of an inventive catalyst system.

When the unsaturated aromatic hydrocarbon is removed prior to introduction to a reactor, the concentrated, or saturated, solution of an inventive catalyst system can be dissolved in a solvent compatible with the trimerization, oligomerization and/or polymerization process to improve ease of handling the inventive catalyst system. Generally, the solvent is the same as the reactor diluent. Preferred solvents include, but are not limited to cyclohexane, isobutane, hexane, pentane, and mixtures thereof.

The reaction, optionally, also can take place in the presence of a halide source. The presence of a halide source in the reaction mixture can increase catalyst system activity and productivity, as well as increase product selectivity. Exemplary halides include, but are not limited to fluoride, chloride, bromide, and/or iodide. Due to ease of use and availability, chloride is the preferred halide. Based

on improved activity, productivity, and/or selectivity, bromide is the most preferred halide.

The halide source can be any compound containing a halogen. Exemplary compounds include, but are not limited to compounds with a general formula of  $R_nX_m$ , wherein R can be any organic and/or inorganic radical, X can be a halide, selected from the group consisting of fluoride, chloride, bromide, and/or iodide, and  $n + m$  can be any number greater than 0. If R is an organic radical, preferably R has from about 1 to about 70 carbon atoms per radical, most preferably from 1 to 20 carbon atoms per radical, for best compatibility and catalyst system activity. If R is an inorganic radical, preferably R is selected from the group consisting of aluminum, silicon, germanium, hydrogen, boron, lithium, tin, gallium, indium, lead, and mixtures thereof. Specific exemplary compounds include, but are not limited to, methylene chloride, chloroform, benzylchloride, silicon tetrachloride, tin (II) chloride, tin (IV) chloride, germanium tetrachloride, boron trichloride, aluminum tribromide, aluminum trichloride, 1,4-di-bromobutane, and/or 1-bromobutane.

Furthermore, the chromium source, the metal alkyl and/or unsaturated hydrocarbon can contain and provide a halide to the reaction mixture. Preferably, the halide source is an alkylaluminum halide and is used in conjunction with alkylaluminum compounds due to ease of use and compatibility, as well as improved catalyst system activity and product selectivity. Exemplary alkylaluminum halides include, but are not limited to, diisobutylaluminum chloride, diethylaluminum chloride, ethylaluminum sesquichloride, ethylaluminum dichloride, diethylaluminum bromide, diethylaluminum iodide, and mixtures thereof.

When a trimerization catalyst system is the desired product, preferably, the reaction mixture

comprises a halide source. Furthermore, most preferably, the halide source is selected from the group consisting of tin (IV) halides, germanium halides, and mixtures thereof. The halide source, most preferably, is combined with the chromium source and pyrrole-containing compound prior to addition of a metal alkyl, i.e., the chromium source and pyrrole-containing compound are pre-treated with a halide source, to increase catalyst system productivity.

The amount of each reactant used to prepare a trimerization catalyst system can be any amount sufficient that, when combined with one or more olefins, trimerization, as defined in this disclosure, occurs. Usually, to prepare a trimerization catalyst system, about one mole of chromium, as the element chromium (Cr), can be combined with about 1 to about 50 moles of pyrrole-containing compound and about 1 to about 75 moles of aluminum, as the element, in an excess of unsaturated hydrocarbon. If an optional halide source is present, usually about 1 to about 75 moles of halide, as the element, are present.

Preferably, about 1 mole of chromium, calculated as the element chromium (Cr), can be combined with about 1 to about 15 moles of pyrrole-containing compound and about 5 to about 40 moles of aluminum, calculated as the element aluminum (Al), in an excess of unsaturated hydrocarbon. If an optional halide source is present, preferably about 1 to about 30 moles of halide, calculated as elemental halide (X), are present. Most preferably, about one mole of chromium, as the element (Cr), is combined with two to four moles of pyrrole-containing compound and 10 to 20 moles of aluminum, as the element (Al), in an excess of unsaturated hydrocarbon. If an optional halide source is present, most preferably 2 to 15 moles of halide, as an element (X), are present.

An excess of pyrrole-containing compound does

not appear to improve, catalyst system activity, productivity, and/or selectivity. An unsaturated hydrocarbon can improve catalyst system stability, activity, and/or selectivity. An excess of the unsaturated hydrocarbon can harm catalyst system selectivity and/or activity. Too much alkylaluminum can decrease catalyst system activity and product selectivity. Too little alkylaluminum can result in incomplete formation of a catalyst system, which in turn, can result in low catalyst system activity and increase formation of undesired polymeric by-products. An excess of an optional halide source can deactivate a catalyst system, and therefore can result in decreased catalyst system activity. As stated earlier, presence of a halide source can increase catalyst system activity and product selectivity.

In accordance with the fourth aspect of the invention preferably the pyrrole-containing compound is present in the reaction mixture together with the metal source prior to the introduction of the metal alkyl. If this order of addition is followed, a better catalyst system, in terms of product selectivity and catalyst system activity and productivity, can be produced.

The reaction preferably occurs in the absence of oxygen, which can deactivate the catalyst, and under anhydrous conditions, i.e., in the initial absence of water. Therefore a dry, inert atmosphere, such as, for example, nitrogen and/or argon is most preferred. Additionally, the metal alkyl is a non-hydrolyzed metal alkyl.

The reaction pressure can be any pressure which does not adversely affect the reaction. Generally, pressures within the range of from about atmospheric pressure to about three atmospheres are acceptable. For ease of operation atmospheric pressure is generally employed.



The reaction temperature can be any temperature. In order to effectuate a more efficient reaction, temperatures which maintain the reaction mixture in a liquid state, for reasons given above, are preferred.

The reaction time can be any amount of time necessary for the reaction to occur. The reaction can be considered a dissolution process; any amount of time which can dissolve substantially all reactants is sufficient. Depending on the reactants, as well as the reaction temperature and pressure, reaction time can vary. Usually, times of less than about 1 day can be sufficient. Usually, reaction time is less than about 60 minutes. Under optimum conditions, the reaction time can be within the range of from about 1 second to about 15 minutes. Longer times usually provide no additional benefit and shorter times may not allow sufficient time for complete reaction.

A heterogeneous, i.e., supported, catalyst system can be prepared in accordance with the fourth aspect of the invention in-situ in the reactor by adding solid support directly to the reactor. As stated earlier, exemplary catalyst supports include, but are not limited to, zeolites, inorganic oxides, either alone or in combination, phosphated inorganic oxides, and mixtures thereof. Particularly preferred are supports selected from the group consisting of silica, silica-alumina, alumina, fluorided alumina, sited alumina, thoria, aluminophosphate, aluminum phosphate, phosphated silica, phosphated alumina, silica-titania, coprecipitated silica/titania, fluorided/sited alumina, and mixtures, thereof, being presently preferred, as well as any one or more of these supports which can contain chromium. The presently most preferred catalyst support, because of the greatest trimerization activity, is aluminophosphate, as disclosed in U.S. Patent

4,364,855. In-situ preparation of a heterogeneous catalyst system, used in a trimerization or oligomerization process, can decrease undesirable formation of polymer.

5 Heterogeneous trimerization, oligomerization, and/or polymerization catalyst systems can also be prepared in accordance with this aspect of the invention by forming a reaction mixture comprising a  
10 chromium source, a pyrrole-containing compound, a metal alkyl, an unsaturated hydrocarbon, and an inorganic oxide, as disclosed earlier. Optionally, as disclosed earlier, a halide source can be added. Reaction stoichiometries and reaction conditions are the same as those disclosed for the second embodiment of the  
15 invention.

Any excess of chromium source, in relation to the inorganic oxide catalyst support, is sufficient. However, usually, less than about 5 grams of chromium  
20 pyrrolide compound per gram of catalyst support is sufficient. Preferably, about 0.001 to about 0.01 to 0.5 gram of chromium pyrrolide compound, or chromium source, per gram of support is used for best support loading and most efficient use of the reagents. The  
25 amount of chromium pyrrolide, or chromium source, compound per gram of support can be expressed in different, yet equivalent terms, such as, for example, moles of chromium per gram of support. Usually, less than about  $8.6 \times 10^{-3}$  moles of chromium per gram of support is sufficient. Preferably, about  $1.7 \times 10^{-4}$  to  
30 about  $1.7 \times 10^{-3}$  to  $8.6 \times 10^{-4}$  moles of chromium per gram of support are used, for reasons given above.

The resultant heterogeneous catalyst system can be collected by filtration, to recover a solid catalyst system product. The solid catalyst system is  
35 preferably kept under a dry, inert atmosphere to maintain chemical stability and reactivity.



describes polymerization catalyst and cocatalyst systems, the cocatalyst including the inventive chromium compounds of Application 60296/90 filed 8 August 1990. Generally, polymerization catalysts systems are  
5 considered either chromium catalysts (also known as "Phillips Catalysts") or titanium, zirconium and/or vanadium-containing catalysts.

Any chromium catalyst system known in the art can be used. Commercially available chromium catalyst  
10 systems typically comprise chromium, at least a portion of which is in the hexavalent state, supported on an inorganic oxide; optionally, the polymerization catalyst system can further comprise a metal alkyl co-catalyst. Exemplary chromium catalyst systems include,  
15 but are not limited to those disclosed in U.S. Patents 3,887,494; 3,900,457; 4,053,436; 4,151,122; 4,294,724; 4,392,990; and 4,405,501.

Any titanium, zirconium and/or vanadium-containing catalyst system known in the art can also be  
20 used. Commercially available titanium, zirconium and/or vanadium catalyst system typically comprise complexes of transition metal halides with organometallic compounds. Exemplary magnesium/titanium catalysts include, but are not limited to, those  
25 disclosed in U.S. Patents 4,394,291; 4,326,988; and 4,347,158.

The amount of novel trimerization and/or oligomerization cocatalyst systems, including the  
30 inventive chromium compounds used as a cocatalyst can be any amount sufficient to generate a comonomer that can be incorporated into the polymer product. The chromium catalyst systems prepared by the various aspects of the present invention can serve as  
35 cocatalysts in conjunction with the titanium, zirconium and/or vanadium-containing catalysts discussed above.

The process of the above fourth aspect of the

invention in combining the metal source, and pyrrole-containing compound, and the metal alkyl, and, preferably an unsaturated hydrocarbon, avoids the need to isolate the first reaction product as per the processes described in our above-mentioned applications. Furthermore, the catalyst systems produced by the process of the fourth aspect of the invention have improved productivity and selectivity to the desired trimerization product, for example in producing one-hexene from ethylene.

#### Polymerization Reactants

Reactants applicable for use in polymerization with the catalyst systems and cocatalyst systems and processes of this invention are olefinic compounds which can polymerize, i.e., react the same or with other olefinic compounds. Catalyst systems of the invention can be used to polymerize at least one linear or branched mono-1-olefin having about 2 to about 8 carbon atoms. Exemplary compounds include, but are not limited to, ethylene, propylene, 1-butene, 1-pentene, 1-hexene, 1-octene, and mixtures thereof.

The catalyst systems of the present invention are also useful in oligomerization processes using olefin compounds having from about 2 to about 30 carbon atoms per molecule and having at least one olefinic double bond. Exemplary mono-olefin compounds include, but are not limited to acyclic and cyclic olefins such as, for example, ethylene, propylene, 1-butene, 2-butene, isobutylene, 1-pentene, 2-pentene, 1-hexene, 2-hexene, 3-hexene, 1-heptene, 2-heptene, 3-heptene, the four normal octenes, the four normal nonenes, and mixtures of any two or more thereof. Exemplary diolefin compounds include, but are not limited to, 1,3-butadiene, isoprene, 1,4-pentadiene, and 1,5-hexadiene. If branched and/or cyclic olefins are used as reactants, while not wishing to be bound by theory, it is believed that steric hindrance could hinder the

trimerization process. Therefore, the branched and/or cyclic portion(s) of the olefin preferably should be distant from the carbon-carbon double bond.

Trimerization, as used in this disclosure, is defined as the combination of any two, three, or more olefins, wherein the number of olefin, i.e., double, bonds is reduced by two. Reactants applicable for use in the trimerization process of this invention are olefinic compounds which can a) self-react, i.e., trimerize, to give useful products such as, for example, the self reaction of ethylene can give one hexene and the self-reaction of 1,3-butadiene can give 1,5-cyclooctadiene; and/or b) olefinic compounds which can react with other olefinic compounds, i.e., co-trimerize, to give useful products such as, for example, co-trimerization of ethylene plus hexene can give one decene and/or 1-tetradecene, co-trimerization of ethylene and 1-butene gives one octene, co-trimerization of 1-decene and ethylene can give 1-tetradecene and/or 1-docosene, or co-trimerization of 1,3-butadiene and 1,5-hexadiene can give 1,5-cyclo-octadecadiene. For example, the number of olefin bonds in the combination of three ethylene units is reduced by two, to one olefin bond, in 1-hexene. In another example, the number of olefin bonds in the combination of two 1,3-butadiene units, is reduced by two, to two olefin bonds in 1,5-cyclooctadiene. As used herein, the term "trimerization" is intended to include dimerization of diolefins, as well as "co-trimerization", both as defined above.

Suitable trimerizable olefin compounds are those compounds having from about 2 to about 30 carbon atoms per molecule and having at least one olefinic double bond. Exemplary mono-olefin compounds include, but are not limited to acyclic and cyclic olefins such as, for example, ethylene, propylene, 1-butene, 2-butene, isobutylene, 1-pentene, 2-pentene, 1-hexene, 2-

hexane, 3-hexene, 1-heptene, 2-heptene, 3-heptene, the four normal octenes, the four normal nonenes, and mixtures of any two or more thereof. Exemplary diolefin compounds include, but are not limited to, 1,3-butadiene, 1,4-pentadiene, and 1,5-hexadiene. If branched and/or cyclic olefins are used as reactants, while not wishing to be bound by theory, it is believed that steric hindrance could hinder the trimerization process. Therefore, the branched and/or cyclic portion(s) of the olefin preferably should be distant from the carbon-carbon double bond.

Catalyst systems produced in accordance with this invention preferably are employed as trimerization catalyst systems.

#### Reaction Conditions

The reaction products, i.e., trimers and/or polymers, can be prepared from the catalyst systems of this invention by solution reactions, slurry reactions, and/or gas phased reaction techniques using conventional equipment and contacting processes. Contacting of the monomer or monomers with the catalyst system or with the polymerization catalyst system and trimerization/oligomerization cocatalyst system, can be effected by any manner known in the art of homogeneous (liquid) or heterogeneous (solid) catalyst systems. One convenient method is to suspend the catalyst system in an organic medium and to agitate the mixture to maintain the catalyst system in suspension throughout the trimerization, oligomerization and/or polymerization process. Other known contacting methods such as fluidized bed, gravitating bed, and fixed bed can also be employed. One convenient method with the catalyst/cocatalyst systems is to suspend a polymerization catalyst system in an organic medium and to agitate the mixture to maintain the polymerization catalyst system in suspension throughout the trimerization and/or polymerization process. An

inventive cocatalyst system can then be added. A polymerization catalyst system and inventive cocatalyst system, preferably, can also be fed simultaneously to a polymerization reactor, via one or more catalyst and/or cocatalyst system feed streams. Other contacting methods such as fluidized bed, gravitating bed, and fixed bed can also be employed with all these catalyst systems.

Reaction temperatures and pressures can be any temperature and pressure which can trimerize, oligomerize, and/or polymerize the olefin reactants. Generally, reaction temperatures are within a range of about 0° to about 250°C. Preferably, reaction temperatures within a range of about 60° to about 200°C. and most preferably, within a range of 80° to 150°C. are employed. Generally, reaction pressures are within a range of about atmospheric to about 2500 psig. Preferably, reaction pressures within a range of about atmospheric to about 1000 psig and most preferably, within a range of 300 to 700 psig are employed.

Too low of a reaction temperature can produce too much undesirable insoluble product and too high of a temperature can cause decomposition of the catalyst system and reaction products. Too low of a reaction pressure can result in low catalyst system activity. Too high of a pressure can cause production of too much undesirable insoluble product.

Optionally, hydrogen can be added to the reactor to accelerate the reaction and/or increase catalyst system activity.

The catalyst systems of this invention are particularly suitable for use in trimerization and/or oligomerizations. The slurry process is generally carried out in an inert diluent (medium), such as a paraffin, cycloparaffin, or aromatic hydrocarbon. Exemplary reactor diluents include, but are not limited to, isobutane and cyclohexane. Isobutane can decrease

the swelling of the polymer product. However, a homogeneous trimerization/oligomerization cocatalyst system is more soluble in cyclohexane. Therefore, a preferred diluent for a homogeneous trimerization or oligomerization process is cyclohexane and a preferred diluent for a heterogeneous trimerization or oligomerization process is isobutane. When the reactant is predominately ethylene, a temperature in the range of about 0° to about 300°C. generally can be used. Preferably, when the reactant is predominately ethylene, a temperature in the range of about 60° to about 150°C. is employed.

Any amount of polymerization catalyst system and cocatalyst system can be present in a polymerization reactor, in order to produce a polymer with a desired set of optimal properties, such as, for example, density, melt index, high load melt index and molecular weight. Usually, up to about 40 parts by weight of a supported, i.e., heterogeneous, cocatalyst system can be present for each part by weight of polymerization catalyst system. Preferably, about 1 to about 25 parts cocatalyst system for each part polymerization catalyst system, and most preferably, 3 to 15 parts by weight cocatalyst system for each part polymerization catalyst system are present, to produce a polymer with desirable physical and processing characteristics.

#### Products

The olefinic and/or polymeric products of this invention have established utility in a wide variety of application such as, for example, as monomers for use in the preparation of homopolymers, copolymers, and/or terpolymers. The polymeric products of this invention have established utility in a wide variety of application such as for example, polyethylene.

The further understanding of the present

invention and its advantages will be provided by reference to the following examples.

Examples

Various, equivalent abbreviations are used throughout the disclosure and examples. Some of these include triethylaluminum as TEA,  $\text{Al}(\text{C}_2\text{H}_5)_3$ ; diethylaluminum chloride as DEAC,  $(\text{Al}(\text{C}_2\text{H}_5)_2\text{Cl})$ ; chromium (III) 2-ethylhexanoate as  $\text{Cr}(\text{EH})_3$ ,  $\text{CrEH}$ ,  $\text{CrEH}_3$ ; hydrogen pyrrolide as pyrrole, Py, PyH,  $(\text{C}_4\text{H}_5\text{N})$ ; chromium (III) acetylacetonate as  $\text{Cr}(\text{acac})_3$ , Cracac<sub>3</sub>, Cracac,  $\text{Cr}(\text{C}_5\text{H}_7\text{O}_2)_3$ ; chromium (III) pyrrolide as  $\text{CrPy}_2$ ,  $[\text{Na}(\text{C}_4\text{H}_9\text{O}_2)_2]$ ,  $[\text{Cr}(\text{C}_4\text{H}_5\text{N})_3\text{Cl}(\text{C}_4\text{H}_9\text{O}_2)]$ ,  $[\text{Na}(\text{DME})_2]$ ,  $[\text{Cr}(\text{C}_4\text{H}_5\text{N})_3\text{Cl}(\text{DME})]$ ,  $[\text{Na}(\text{DME})_2]$ ,  $[\text{Cr}(\text{Py})_3\text{Cl}(\text{DME})]$ , Product V, Compound V; chromium (III) chloride tris-tetrahydrofuran as  $\text{CrCl}_3\text{THF}_3$ ,  $\text{CrCl}_3(\text{THF})_3$ ; 2,5-dimethylpyrrole as, hydrogen 2,5-dimethylpyrrolide,  $\text{C}_6\text{H}_9\text{N}$ , 2,5-DMP; butene as  $\text{C}_4=$ ; 1-hexene as 1- $\text{C}_6=$ ; hexene as  $\text{C}_6=$ ; octene as  $\text{C}_8=$ ; decene as  $\text{C}_{10}=$ ; dodecene as  $\text{C}_{12}=$ ; tetradecene as  $\text{C}_{14}=$ .

Example I

Run 1001

0.14 g (0.29 mmol) of chromium (III) 2-ethylhexanoate ( $\text{CrEH}_3$ ,  $[\text{Cr}(\text{C}_8\text{H}_{15}\text{O}_2)_3]$ , was weighed into a 25 ml pressure tube. The tube was capped with a self sealing crown cap. 0.062 ml (0.89 mmol) pyrrole (PyH),  $[\text{C}_4\text{NH}_5]$  and cyclohexane, used as a diluent, were added via syringe to form a solution, which was about 8 ml total volume.

0.9 ml of a 1.1 M solution (0.99 mmol) of triethylaluminum (TEA),  $[\text{Al}(\text{C}_2\text{H}_5)_3]$ , in heptane and a 0.9 ml aliquot of the  $\text{CrEH}_3/\text{PyH}$  solution were added under a counterflow of ethylene (CP grade) to a 1 liter autoclave reactor, containing 300 mL cyclohexane, to form a catalyst system. The reactor was sealed and ethylene addition stopped until the reactor temperature reached a reaction temperature of 80°C. The ethylene pressure was increased to a total reactor pressure of



550 psig. Ethylene was then fed on demand for a 30 minute run time. At the end of the run, a sample of the liquid reaction product mixture was taken and analyzed via capillary gas chromatography. The remaining reaction product mixture was evaporated and the amount of solid product was determined. The results are summarized below in Table XXIII.

#### Run 1002

The procedure described in Run 1001 was followed except 8 ml of a 1.1 M solution (8.8 mmol) of TEA in heptane was added directly to the  $\text{CrEt}_2/\text{PyH}$  solution to form a solution (10 ml total volume) and not to the reactor. A 0.7 ml aliquot of the  $\text{CrEt}_2/\text{PyH}/\text{TEA}$  solution was added to the autoclave reactor. No additional TEA was introduced into the reactor. The results are summarized below in Table XXIII.

#### Run 1003

The procedure described in the Run 1002 was followed except 0.10g (0.29 mmol) chromium (III) acetylacetonate ( $\text{Cracac}_3$ ),  $[\text{Cr}(\text{C}_5\text{H}_7\text{O}_2)_3]$ , was substituted for  $\text{CrEt}_2$  and 6 ml of a 1.1 M solution TEA (6.6 mmol) in heptane was used in the formation of a  $\text{Cracac}_3/\text{PyH}/\text{TEA}$  solution (8 ml total volume). A 1.4 ml aliquot of the  $\text{Cracac}_3/\text{PyH}/\text{TEA}$  solution was added to the autoclave reactor. The results are summarized below in Table XXIII.

#### Run 1004

The procedure described in Run 1001 was followed except 0.9 ml of a 1 M solution (0.9 mmol) of diethylaluminum chloride (DEAC),  $[\text{AlCl}(\text{C}_2\text{H}_5)_2]$ , in hexanes was added to the  $\text{CrEt}_2/\text{PyH}$  solution to form a  $\text{CrEt}_2/\text{PyH}/\text{DEAC}$  solution. A 0.65 ml aliquot of the  $\text{CrEt}_2/\text{PyH}/\text{DEAC}$  solution and 0.9 ml of a 1.1 M solution (0.99 mmol) of TEA in heptane were added to the autoclave reactor. The results are summarized below in Table XXIII.



Run 1005

The procedure described in Run 1001 was followed except 0.9 ml of a 1 M solution (0.9 mmol) of DEAC in hexanes was added to the CrEH<sub>2</sub>/PyH solution and the resultant CrEH<sub>2</sub>/PyH/DEAC solution was aged for 1 day at ambient temperature and pressure, under dry nitrogen. A 0.65 ml aliquot of the aged CrEH<sub>2</sub>/PyH/DEAC solution + 0.9 ml of a 1.1 M solution (0.99 mmol) of TEA in heptane were added to the autoclave reactor. The results are summarized below in Table XXIII.

Run 1006

The procedure described in Run 1001 was followed except a solution was prepared using 0.13 ml pyrrole. Additionally, 1.0 ml of a 0.1 M solution (0.1 mmol) of DEAC in hexanes was added along with the TEA to the reactor. A 0.9 ml aliquot of the CrEH<sub>2</sub>/PyH solution was used. The results are summarized below in Table XXIII.

Run 1007

The procedure described in Run 1003 was followed except 3 ml of a 1.9 M solution (5.7 mmol) of TEA in toluene was used and toluene was substituted for the cyclohexane diluent in the formation of the CrEH<sub>2</sub>/PyH/TEA solution. Thus, an excess of toluene was present in the reactor. A 0.9 ml aliquot of the CrEH<sub>2</sub>/PyH/TEA solution was used. The results are summarized below in Table XXIII.

Run 1008

The procedure described in Run 1002 was followed except 0.10 g of a chromium (III) pyrrolide (CrPy<sub>3</sub>), [Cr(C<sub>4</sub>H<sub>7</sub>N)<sub>3</sub>ClNa(C<sub>4</sub>H<sub>10</sub>O<sub>2</sub>)<sub>3</sub>] (0.17 mmol) was substituted for CrEH<sub>2</sub>, and a solution was prepared using 0.04 ml (0.52 mmol) PyH and 3.5 ml of a 1.1 M TEA (3.85 mmol) in heptanes. The final solution volume was about 5 ml. A 1.0 ml aliquot of the CrPy<sub>3</sub>/PyH/TEA solution was used. The results are summarized below in Table XXIII.

Run 1009

The procedure described in Run 1008 was followed except 1.8 ml of a 1.9 M TEA solution (3.42 mmol) in toluene was used, and toluene was substituted  
5 for cyclohexane in the formation of the CrPy<sub>2</sub>/PyH/TEA solution. Thus, an excess of toluene was present in the reactor. A 1.4 ml aliquot of the CrPy<sub>2</sub>/PyH/TEA solution was used. The results are summarized below in Table XXIII.

10

Run 1010

The procedure described in Run 1008 was followed except no neat PyH was added during the preparation of a CrPy<sub>2</sub>/TEA solution. A 1.4 ml aliquot of the CrPy<sub>2</sub>/TEA solution, in cyclohexane, was used.

15

The results are summarized below in Table XXIII.

Run 1011

The procedure described in Run 1009 was followed except no neat PyH was added during the preparation of a CrPy<sub>2</sub>/TEA solution. A 1.4 ml aliquot  
20 of the CrPy<sub>2</sub>/TEA solution, in toluene, was used. Thus, an excess of toluene was present in the reactor. The results are summarized below in Table XXIII.

Table XXIII

## Homogeneous Catalyst Systems

Run	mg Cr (elemental) Charged	Activity (g product/ g Cr/hr)	Total Product Yield, g	Wt. % Liquid Solid	Liquid Product Distribution, Weight Percent				
					C <sub>4</sub> = 1-C <sub>4</sub> =	C <sub>5</sub> =	C <sub>6</sub> =	C <sub>10</sub> =	C <sub>12</sub> = C <sub>14</sub> =
1001	1.6	11,000	8.8	94	2	-	89*	2	6 <1 <1
1002	0.96	8,800	4.2	88	12	1	87	5	2 4 <1 <1
1003	2.6	9,800	12.8	64	36	2	81	4	4 5 1 1
1004	1.1	15,000	8.5	98	2	<1	-	92*	1 6 <1 <1
1005	1.1	26,000	14.9	98	2	<1	88	4	6 <1 <1 <1
1006	1.5	12,000	9.0	98	2	<1	-	97*	1 2 <1 <1
1007	2.6	3,500	4.6	50	50	2	86	4	3 3 <1 <1
1008	2.5	8,300	10.5	>99	<1	1	83	5	<1 8 <1 1
1009	2.5	4,100	5.2	99	1	1	88	4	1 1 6 <1 <1
1010	2.5	7,100	8.9	97	3	<1	82	6	1 8 <1 1
1011	2.5	3,300	4.2	98	2	<1	89	4	1 5 <1 <1

\* Total hexenes.

Example II

It should be noted that the results in Table XXIII, from Example X, and the results in Table XXIV, from Example XI, are not directly comparable, due to reactions conducted in different reactors, under different conditions, by the use of different ethylene and cyclohexane feedstocks, as well as different diluents. However, direct comparisons within each Example can be made.

Run 2001

0.30 g (0.62 mmol) of chromium (III) 2-ethylhexanoate ( $\text{CrEH}_2$ ) (10.15 wt% Cr) was combined with 0.12 ml (1.73 mmole) of neat pyrrole (PyH) in 10 ml of toluene. 2.8 ml of 1.9 M triethylaluminum (TEA) solution (5.32 mmol) in toluene was added, and the  $\text{CrEH}_2$ /PyH/TEA solution was stirred for 30 minutes under dry nitrogen, at ambient temperature and pressure. The dark brown  $\text{CrEH}_2$ /PyH/TEA solution was filtered and excess toluene was removed by vacuum stripping, which resulted in 1.0 ml of a dark brown oil, used as catalyst system. Under a counterflow of ethylene, 0.5 ml (0.15g  $\text{CrEH}_2$ , 15.2 mg Cr) of the catalyst system and 4.0 ml of nonane (reactor internal standard) were added to a 2 liter autoclave reactor at 80°C., which contained 1.2 liters of cyclohexane. The reactor was then pressurized with ethylene to 550 psig, and the reaction was run for 30 minutes, with ethylene being fed on demand.

The results are summarized below in Table XXIV.

Run 2002

The procedure described in Run 2001 was followed except diethylaluminum chloride was added in addition to the  $\text{CrEH}_2$ /PyH/TEA solution.

0.53 g (1.10 mmol) of  $\text{CrEH}_2$  (10.15 wt. % Cr) was combined with 0.52 ml (7.5 mmole) of neat PyH in 15 ml of toluene and stirred for 5 min. 9.0 ml of a 1.9 M

TEA solution (17.1 mmol) in toluene was added, and the  $\text{CrEt}_2/\text{PyH}/\text{TEA}$  solution was stirred overnight under dry nitrogen at ambient temperature and pressure. Excess toluene was removed from the resultant dark brown solution via vacuum stripping, which resulted in 2.5 ml of a dark brown oil. 0.5 ml (10.8 mg; 0.21 mmole Cr) of the dark brown oil was combined with 1.0 ml of a 0.87 M (0.87 mmol) diethylaluminum chloride (DEAC) solution in nonane, and the  $\text{CrEt}_2/\text{PyH}/\text{TEA}/\text{DEAC}$  solution was stirred overnight under dry nitrogen, at ambient temperature and pressure. The resultant product was used as the catalyst system. Under a counterflow of ethylene, 1.3 ml (9.4 mg Cr; 0.18 mmole Cr) of the catalyst system and 4.0 ml of nonane (reactor internal standard) were charged directly to a 2 liter reactor at 80°C., which contained 1.2 liters of cyclohexane. The reactor was then pressurized with ethylene to 550 psig, and the reaction was run for 30 minutes with ethylene being fed on demand.

The results are summarized below in Table XXIV.

Run 2003

0.33 g (0.68 mmol) of  $\text{CrEt}_2$  (10.15 wt. % Cr) was combined with 0.13 ml (1.87 mmole) of neat PyH in 10 ml of toluene and stirred 5 min. 1.9 ml of a 1 M (1.9 mmol) DEAC solution in hexanes was added and the  $\text{CrEt}_2/\text{PyH}/\text{DEAC}$  solution was stirred for 30 minutes under dry nitrogen, at ambient temperature and pressure, which resulted in a light yellow/green solution. 5.1 ml of a 1.9 M (9.7 mmol) diethylaluminum chloride (DEAC) solution in toluene was added, and the  $\text{CrEt}_2/\text{PyH}/\text{DEAC}/\text{TEA}$  solution was stirred for 0.5 hr, which resulted in a dark yellow/brown solution. Excess toluene and hexane was removed from the dark yellow/brown  $\text{CrEt}_2/\text{PyH}/\text{DEAC}/\text{TEA}$  solution via vacuum stripping, with a dark yellow/brown oil remaining. The yellow/brown oil was dissolved and brought to a total

volume of 25 ml in cyclohexane and used as a catalyst system (1.32mg Cr/ml). Under a counterflow of ethylene, 7.0ml (9.2mg Cr; 0.178 mmole Cr) of the catalyst system and 4.0 ml of nonane (reactor internal standard) were charged directly to a 2 liter reactor at 80°C., which contained 1.2 liters of cyclohexane. The reactor was then pressurized with ethylene to 550 psig and the reaction was run for 30 minutes with ethylene being fed on demand.

The results are summarized below in Table XXIV.

#### Run 2004

The procedure described in Run 2002 was followed, except the  $\text{CrEt}_2/\text{PyH}/\text{TEA}/\text{DEAC}$  solution was diluted with cyclohexane prior to charging to the reactor, and dihydrogen gas ( $\text{H}_2$ ) (50 psig) was added to the reactor prior to pressurizing the reactor with ethylene.

0.30 g (0.62 mmol) of  $\text{CrEt}_2$  (10.15% Cr) was combined with 0.12 ml (1.73 mmole) of neat PyH in 10 ml of toluene. 1.7 ml of a 1 M (1.7 mmol) DEAC solution in hexanes was added and the  $\text{CrEt}_2/\text{PyH}/\text{DEAC}$  solution was stirred for 5 minutes under dry nitrogen, at ambient temperature and pressure. 1.8 ml of a 1.9 M (3.42 mmol) TEA solution in toluene was added and the  $\text{CrEt}_2/\text{PyH}/\text{DEAC}/\text{TEA}$  solution was stirred for 30 minutes under dry nitrogen, at ambient temperature and pressure. The resultant dark brown solution was filtered and excess toluene and hexanes were removed via vacuum stripping, which resulted in 0.8 ml of a dark yellow/brown oil and was used as a catalyst system. Under a counterflow of ethylene, 0.4ml (15.2mg Cr; 0.29 mmole Cr) of the catalyst system and 4.0 ml of nonane (reactor internal standard) were charged directly to the 2 liter reactor at 80°C., which contained 1.2 liters of cyclohexane. 50 psig of dihydrogen ( $\text{H}_2$ ) gas was charged to the reactor, followed



by pressurization with ethylene to 550 psig. The reaction was run for 30 minutes with ethylene being fed on demand.

The results are summarized below in Table

5 XXIV.

Run 2005

In a 500 ml Schlenk flask 1.98 g (3.4 mmol) of CrPy<sub>3</sub> (11.1 wt. % Cr) was combined with 40 ml of toluene and 54 ml of a 1.9 M (102.6 mmol) TEA solution  
10 in toluene. The resulting dark brown reaction mixture was stirred for 1 hour under dry nitrogen, at ambient temperature and pressure. Excess toluene was removed via vacuum stripping, which resulted in 13 ml of a dark  
15 yellow/brown oil and a small quantity of a light-colored precipitate. The dark yellow/brown oil was separated, collected by syringe from the precipitate, and used as the catalyst system. 2.0 ml of the catalyst system was diluted with 27 ml of cyclohexane  
20 and aged for 3 days under dry nitrogen, at ambient temperature and pressure before using.

Under a counterflow of ethylene, 8.0 ml (9.3mg; 0.18 mmole Cr) of the catalyst system/cyclohexane solution and 4.0 ml of nonane (reactor internal standard) were charged directly to a  
25 2 liter autoclave reactor at 80°C., which contained 1.2 liters of cyclohexane. The reactor was then pressurized with ethylene to 550 psig and the reaction was run for 30 minutes with ethylene being fed on demand.

30 The results are summarized below in Table XXIV.

Run 2006

The procedure described in Run 2005 was followed except less reactants were used and less aging  
35 time was used.

In a 500 ml Schlenk flask 0.25 g (0.432 mmol) of CrPy<sub>3</sub> (11.1 wt. % Cr) was combined with 10 ml of

toluene and 3.4 ml of a 1.9 M (6.46 mmol) TEA solution in toluene. The resulting dark brown reaction mixture was stirred for 30 minutes under dry nitrogen, at ambient temperature and pressure. Excess toluene was removed via vacuum stripping, which resulted in a dark brown oil. All of the dark brown oil was diluted to a total volume of 25 ml with cyclohexane, resulting in a solution containing 1.11 mg Cr/ml, which was used as the catalyst system.

Under a counterflow of ethylene, 8.0 ml (8.88 mg; 0.171 mmole Cr) of the catalyst system/cyclohexane solution and 4.0 ml of nonane (reactor internal standard) were charged directly to a 2 liter autoclave reactor at 80°C., which contained 1.2 liters of cyclohexane. The reactor was then pressurized with ethylene to 550 psig and the reaction was run for 30 minutes with ethylene being fed on demand.

The results are summarized below in Table XXIV.

Run 2007

The procedure described in Run 2005 was followed except excess toluene was present in the trimerization reactor.

In a 500 ml Schlenk flask 1.98 g (3.4 mmol) of CrPy<sub>3</sub> (11.1 wt. % Cr) was combined with 40 ml of toluene and 54 ml of a 1.9 M (102.6 mmol) TEA solution in toluene. The resulting dark brown reaction mixture was stirred for 1 hour under dry nitrogen, at ambient temperature and pressure. Excess toluene was removed via vacuum stripping, which resulted in 13 ml of a dark yellow/brown oil and a small quantity of a light-colored precipitate. The dark yellow/brown oil was separated, collected by syringe from the precipitate, and used as the catalyst system. 2.0 ml of the catalyst system was diluted with 27 ml of cyclohexane and aged for 3 days under dry nitrogen, at ambient temperature and pressure before using.



Under a counterflow of ethylene, 0.5 ml (8.5 mg; 0.163 mmole Cr) of the catalyst system/cyclohexane solution, 4.5 ml of toluene, and 4.0 ml of nonane (reactor internal standard) were charged directly to a 2 liter autoclave reactor at 80°C., which contained 1.2 liters of cyclohexane. The reactor was then pressurized with ethylene to 550 psig and the reaction was run for 30 minutes with ethylene being fed on demand.

10 The results are summarized below in Table XXIV.

Run 2008

0.28 g (0.802 mmol) of Cracac<sub>3</sub> was combined with 0.17 ml (2.45 mmol) of neat pyrrole in 10 ml of toluene and stirred under dry nitrogen, at ambient temperature and pressure for 5 minutes. Then, 6.3 ml of a 1.9 M (12.0 mmol) TEA solution in toluene was added. The resulting dark brown reaction mixture was stirred for 30 minutes under dry nitrogen, at ambient temperature and pressure. Excess toluene was removed via vacuum stripping, which resulted in a dark yellow/brown oil. All of the dark yellow/brown oil was diluted to a volume of 25 ml with cyclohexane, resulting in a solution containing 0.0112g Cracac<sub>3</sub>/ml, which was used as the catalyst system.

Under a counterflow of ethylene, 7.0 ml (15.2 mg; 0.293 mmole Cr) of the catalyst system/cyclohexane solution and 4.0 ml of nonane (reactor internal standard) were charged directly to a 2 liter autoclave reactor at 80°C., which contained 1.2 liters of cyclohexane. The reactor was then pressurized with ethylene to 550 psig and the reaction was run for 30 minutes with ethylene being fed on demand.

35 The results are summarized below in Table XXIV.

Run 2009

The procedure described in Run 2008 was

followed except chromium (III) naphthenate was the chromium source.

0.33 g (0.508 mmol) of CrNaph<sub>3</sub> (8.0 wt. % Cr) was combined with 0.12 (1.73 mmol) of neat pyrrole in 10 ml of toluene and stirred under dry nitrogen at ambient temperature and pressure for 5 minutes. Then, 4.6 ml of a 1.9 M (8.74 mmol) TEA solution in toluene was added. The resulting dark brown reaction mixture was stirred for 30 minutes under dry nitrogen, at ambient temperature and pressure. Excess toluene was removed via vacuum stripping, which resulted in a dark yellow/brown oil. All of the dark yellow/brown oil was diluted to a total volume of 25 ml with cyclohexane, resulting in a solution containing 1.056 mg Cr/ml, which was used as the catalyst system.

Under a counterflow of ethylene, 7.0 ml (7.39 mg; 0.142 mmole Cr) of the catalyst system/cyclohexane solution and 4.0 ml of nonane (reactor internal standard) were charged directly to a 2 liter autoclave reactor at 80°C., which contained 1.2 liters of cyclohexane. The reactor was then pressurized with ethylene to 550 psig and the reaction was run for 30 minutes with ethylene being fed on demand.

The results are summarized below in Table XXIV.

#### Run 2010

The procedure described in Run 2008 was followed except the chromium (III) chloride was the chromium source.

0.41 g (1.09 mmol) of CrCl<sub>3</sub>·THF<sub>3</sub> was combined with 0.23 ml (3.32 mmol) of neat pyrrole in 10 ml of toluene and stirred under dry nitrogen, at ambient temperature and pressure for 5 minutes. Then 8.6 ml of a 1.9 M (16.3 mmol) TEA solution in toluene was added. The resulting dark brown reaction mixture was stirred for 30 minutes under dry nitrogen, at ambient temperature and pressure. Excess toluene was removed

via vacuum stripping, which resulted in a dark yellow/brown oil. 7.5 ml of nonane was added to the dark yellow/brown oil and the resultant solution was diluted to a total volume of 25 ml with cyclohexane, resulting in a solution containing 0.0164 g  $\text{CrCl}_3\text{THF}/\text{ml}$ . The solution was filtered and the filtrate was used as the catalyst system.

Under a counterflow of ethylene, 5.0 ml (11.38 mg; 0.219 mmole Cr) of the catalyst system/cyclohexane/nonane solution and 2.5 ml of nonane (reactor internal standard) were charged directly to a 2 liter autoclave reactor at 80°C., which contained 1.2 liters of cyclohexane. The reactor was then pressurized with ethylene to 550 psig and the reaction was run for 30 minutes with ethylene being fed on demand.

The results are summarized below in Table XXIV.

Run 2011

The procedure described in Run 2005 was followed except excess hexene was charged to the trimerization reactor.

In a 500 ml Schlenk flask, 1.98 g (3.4 mmol) of  $\text{CrPy}_3$  (11.1 wt. % Cr) was combined with 40 ml of toluene and 54 ml of a 1.9 M (102.6 mmol) TEA solution in toluene. The resulting dark brown reaction mixture was stirred for 1 hour under dry nitrogen, at ambient temperature and pressure. Excess toluene was removed via vacuum stripping, which resulted in 13 ml of a dark yellow/brown oil and a small quantity of a light-colored precipitate. The dark yellow/brown oil was separated, collected by syringe from the precipitate, and used as the catalyst system. 2.0 ml of the catalyst system was diluted with 27 ml of cyclohexane and aged for 3 days under dry nitrogen, at ambient temperature and pressure before using.

Under a counterflow of ethylene, 1.0 ml (16.9

mg; 0.325 mmole Cr) of the catalyst system/cyclohexane solution, 55 ml of 1-hexene, and 4.0 ml of nonane (reactor internal standard) were charged directly to a 2 liter autoclave reactor at 80°C., which contained 1.2  
5 liters of cyclohexane. The reactor was then pressurized with ethylene to 550 psig and the reaction was run for 30 minutes with ethylene being fed on demand.

The results are summarized below in Table

10 XXIV.

Run 2012

The procedure described in Run 2005 was followed except chromium (II) pyrrolide (Compound I) was the chromium source.

15 0.30 g (about 0.85 mmol) of Compound I ( $\text{CrPy}_{10}\text{THF}_4$ ) was combined with 10 ml of toluene and 6.7 ml of a 1.9 M (12.7 mmol) TEA solution in toluene. The resulting dark brown reaction mixture was stirred for 30 minutes under dry nitrogen, at ambient temperature  
20 and pressure. Excess toluene was removed via vacuum stripping, which resulted in a dark yellow/brown oil and a small quantity of a light-colored precipitate. The dark yellow/brown oil was filtered and the filtrate was diluted to a total volume of 25 ml with  
25 cyclohexane, resulting in a solution containing 0.012 g Compound I ( $\text{CrPy}_{10}\text{THF}_4$ ), which was used as the catalyst system.

Under a counterflow of ethylene, 7.0 ml of the catalyst system/cyclohexane solution and 4.0 ml of  
30 nonane (reactor internal standard) were charged directly to a 2 liter autoclave reactor at 80°C., which contained 1.2 liters of cyclohexane. The reactor was then pressurized with ethylene to 550 psig and the reaction was run for 30 minutes with ethylene being fed  
35 on demand.

The results are summarized below in Table

XXIV.

Table XXIV

## Catalyst Systems With Solvent Removal

Run	mg Cr (Elemental) Charged	Molar Ratio Cr:Py: TEA:DEAC	Acti- vity (g pro- duct/ g Cr/hr)	Total Product Yield, g	Wt. % Liquid Solid	Liquid Product Distribution						
						Weight Percent						
						C <sub>1</sub> =	1-C <sub>1</sub> =	C <sub>2</sub> =	C <sub>3</sub> =	C <sub>4</sub> =	C <sub>10</sub> =	C <sub>12</sub> =
2001	15.2	1:3:9:0	4,000	30.5	74	26	9	53	2	9	5	4
2002	9.3	1:7:15.5:4	6,000	23.2	95	5	<1	88	4	2	3	<1
2003	9.2	1:3:15:3	8,300	38.5	88	12	<1	86	3	2	5	<1
2004	15.2	1:3:6:3	4,900	37.0	96	4	<1	91	2	2	3	<1
2005	7.5	1:3:30:0	10,600	40.0	98	2	<1	82	9	1	7	<1
2006	7.2	1:3:15:0	10,800	38.9	97	3	<1	81	5	3	7	<1
2007	6.8	1:3:30:0	1,100	3.2	94	6	4	84	6	1	4	<1
2008	11.8	1:3:15:0	17,000	98.9	95	5	<1	84	5	1	6	<1
2009	7.4	1:3:15:0	15,700	57.8	72	28	<1	88	2	2	5	<1
2010	11.4	1:3:15:0	8,000	45.3	98	2	<1	88	4	1	5	<1
2011 1	13.7	1:30:0:0	4,600	31.3	-	-	-	<1	76	11	1	10
2012	10.0	1:2:18.5:0	8,800	44.1	99	1	<1	77	9	1	11	<1

Example III

Run 3001

0.21g (0.601 mmol) of Cracac<sub>3</sub> was combined with 0.12 ml (1.73 mmol) of neat pyrrole and 15 ml of toluene. The resulting solution was stirred under dry nitrogen, at ambient temperature and pressure for 5 minutes. Then, 6.0 ml of a 1.9 M (11.4 mmol) TEA solution in toluene was added. The resulting dark brown reaction mixture was stirred for 5 minutes under dry nitrogen, at ambient temperature and pressure. Then, 2.0 g of an aluminophosphate support (0.4 P/Al molar ratio, activated at 700°C.), prepared in accordance with U.S. 4,364,855 (1982), herein incorporated by reference, was added and the resulting slurry stirred for a period of approximately 12 hours. The product was collected by filtration, rinsed at least twice with 10 ml aliquots of toluene and pentane, until no color was observed in the filtrate and vacuum dried. The dried product was used as solid supported catalyst system.

A 2.1022 g aliquot of the solid catalyst system was added under a counterflow of ethylene to a 2 liter autoclave containing 1 liter of isobutane. Prior to the catalyst charge, 0.25 ml of a 16.5 wt% TEA solution in nonane was added to the reactor, in order to neutralize any ethylene feedstock poisons that might be present. The reactor was sealed and ethylene addition was stopped until the reactor temperature reached the desired run temperature, for example 90°C. The ethylene pressure was then increased to a total reactor pressure of 550 psig. Ethylene was fed on demand for a 30 minute run time. At the end of the run, a sample of the liquid reaction product mixture was collected and analyzed via gas chromatography. The remaining reaction mixture was evaporated and the amount of solid product was determined.

The results are summarized in Table XXV.



Run 3002

The procedure described in Run 3001 was followed except diethylaluminum chloride was added to the Cracac/PyH solution along with the TEA prior to the aluminophosphate inorganic oxide addition.

0.21 g Cracac<sub>3</sub> (0.60 mmol) was weighed into a 30 ml screw-capped vial. 0.12 ml of PyH (1.73 mmol) and 15 ml of toluene were added, and the resulting solution was capped and stirred for 5 minutes. Then, with continued stirring, 6 ml of a 1.9 M (11.4 mmol) TEA solution in toluene was added. After the Cracac/PyH/TEA solution was stirred for 5 minutes, 2.4 ml of a 1 M (2.4 mmol) DEAC solution in hexanes was added and the Cracac/PyH/TEA/DEAC/toluene solution was stirred for 5 minutes. 2.0 g of an aluminophosphate support (0.4 P/Al molar ratio, activated at 700°C.), prepared in accordance with U.S. 4,364,855 (1982), herein incorporated by reference, was added and the resulting slurry stirred for a period of approximately 12 hours. The product was collected by filtration and rinsed with at least two 10 ml aliquots of toluene and pentane, until no color was observed in the filtrate, and vacuum dried. The dried product was used as a solid, supported catalyst system.

A 0.5048 g aliquot of the solid catalyst system was added under a counterflow of ethylene to a 2 liter autoclave containing 1 liter of isobutane. Prior to the catalyst charge, 3.0 ml of a 1.6 wt% TEA solution in nonane was added in order to neutralize any ethylene feedstock poisons that might be present. The reactor was sealed and ethylene addition stopped until the reactor temperature reached the desired run temperature, for example 90°C. The ethylene pressure was increased to a total reactor pressure of 550 psig. Ethylene was then fed on demand for a 30 minutes run time. At the end of the run, a small sample of the liquid reaction product mixture was collected and

analyzed via gas chromatography. The remaining reaction mixture was evaporated and the amount of solid product determined. Ethylene consumption was determined by a calibrated flow meter.

5           The results are summarized below in Table XXV.

Run 3003

10           The procedure described in Run 3002 was followed except  $\text{CrEH}_3$  was the chromium source and no aromatic solvent was used during catalyst system preparation. Also, a supported catalyst system was prepared in-situ in the reactor.

15           A  $\text{CrEH}_3/\text{PyH}$  solution was prepared by mixing 0.33 g (0.69 mmole)  $\text{CrEH}_3$  with 0.26 ml (3.75 mmole)  $\text{PyH}$  in 16 ml of pentane and aging for 4 days under dry nitrogen, at ambient temperature and pressure, prior to usage. 0.49 g of an aluminophosphate support (0.9 P/Al molar ratio, activated at 700°C.), prepared in accordance with U.S. 4,364,855 (1982), herein  
20           incorporated by reference, and 2.0 ml of a 1 M (2.0 mmol) TEA solution in hexanes were charged under a counterflow of ethylene to a 2 liter autoclave reactor at ambient temperature. Then, 1 liter of cyclohexane, 2.1 ml (4.32mg; 0.083 mmole Cr) of the  $\text{CrEH}_3/\text{PyH}$   
25           solution, and 50 psig dihydrogen gas ( $\text{H}_2$ ) were charged to the reactor.

          The results are summarized below in Table XXV.



Table XXV

Run	Grams Catalyst System	Molar Ratio Cr:Py: TEA:DEAC	Activity (g prod/g Total catalyst/ hr)	Yield, g Product	Wt. % Liquid	Wt. % Solid	Liquid Product Distribution, Weight Percent					
							C <sub>1</sub> =	1-C <sub>1</sub> =	C <sub>2</sub> =	C <sub>3</sub> =	C <sub>10</sub> =	C <sub>12</sub> =
3001	2.1022	-	210	223	82	18	1	76	7	2	11	1
3002	0.5048	1:3:19:4	340	87	99	1	1	82	7	1	8	<1
3003	0.0426 <sup>a</sup>	1:5.5:22.6:0	450	224	88	12	6	61	6	5	13	2

a) Grams of only Cr(EH), charged; mass of other catalyst system components are excluded.

Example IV

Run 4001

3.5 g (10 mmol) Cracac<sub>3</sub> was weighed into a 100 ml pressure tube. A stir bar was placed in the tube and the tube was capped with a self sealing crown cap. 40 ml toluene and 2.1 ml (30 mmol) PyH were added via syringe. 12 ml of a 2.5 M (30.0 mmol) n-butyl lithium solution in hexanes was slowly added. A precipitate was formed, collected, and washed with one 10 ml aliquot of toluene and two 10 ml aliquots of cyclohexane, until no color was observed in the wash solution. A total of 5.59 g solid was obtained. 0.5 ml of a 1.1 M (0.55 mmol) TEA solution in heptane and a slurry of 38 mg of the solid and cyclohexane were used in a reaction under the conditions described in Run 1001.

The results are summarized below in Table XXVI.

Example 4002

The procedure described in Run 4001 was followed except the solid catalyst component (88 mg collected) was prepared in a 25 ml pressure tube using 0.349 g (1 mmol) Cracac<sub>3</sub>, 5 ml toluene, 0.14 ml (2 mmol) PyH, and 0.8 ml of a 2.5 M (2.0 mmol) n-butyl lithium solution in hexane.

0.5 ml of a 1.1 M (0.55 mmol) TEA solution in heptanes and a cyclohexane slurry containing 16 mg of the solid were used in a reaction under the conditions described in Run 1001.

The results are summarized below in Table XXVI.

Run 4003

1.0 g of aluminophosphate support (0.4 P/Al molar ratio, activated 700°C.), prepared in accordance with U.S. 4,364,855 (1982), herein incorporated by reference, and an 93 mg aliquot of the solid described in Run 4001, were weighed into a 25 ml pressure tube.

The tube was capped. 5 ml toluene and 3 ml of a 1.9 M (5.7 mmol) TEA solution in toluene were added to the tube via syringe. The resulting slurry was agitated for one day. The solid was isolated and washed with 10 ml aliquots of toluene and cyclohexane until no color was observed in the wash solution.

0.5 ml of a 1.1 M (0.55 mmol) TEA solution in heptanes and a cyclohexane slurry containing 80 mg of the solid were used in a reaction under the conditions described in Run 1001.

The results are summarized below in Table XXVI.

Run 4004

0.7 g of aluminophosphate support (0.4 P/Al molar ratio, activated at 700°C.), prepared in accordance with U.S. 4,364,855 (1982), herein incorporated by reference, and an aliquot (53 mg) of the solid described in Run 4002 were weighed into a 25 ml pressure tube. The tube was capped. 3.5 ml toluene and 2 ml of a 1.9 M (3.8 mmol) TEA solution in toluene were added to the tube via syringe. The resulting slurry was agitated for one day. The solid was isolated and washed with 10 ml aliquots of toluene and cyclohexane until no color was observed in the wash solution.

0.5 ml of a 1.1 M (0.55 mmol) TEA solution in heptane and a cyclohexane slurry containing 78 mg of the solid were used in a reaction under the conditions as described in Run 1001.

The results are summarized below in Table XXVI.

Table XXVI

## Lithium-Alkyls in Catalyst Preparation

Run	Grams Catalyst Charged	Activity (g prod./g Cat./hr)	Total Product Yield, g	Wt. % Liquid Solid	Wt. % Liquid	Liquid Product Distribution, Weight Percent				
						C <sub>1</sub> =	1-C <sub>4</sub> =	C <sub>6</sub> =	C <sub>10</sub> =	C <sub>12</sub> =
4001	0.038	95	1.8	86	14	4	81	5	3	<1
4002	0.016	540	4.3	82	18	3	83	5	3	<1
4003	0.080	110	4.3	89	11	1	79	5	3	2
4004	0.078	310	12.2	84	16	1	78	6	2	1

Example V

Run 5001

0.17 g chromium (III) 2,2,6,6-tetramethyl-3,5-heptanedionate (Cr(III)TMHD) (0.28 mmol) was weighed into a 25 ml pressure tube. The tube was capped with a self sealing crown cap. 0.06ml of pyrrole (0.89 mmol) and 0.17 ml of neat (0.87 mmol) diisobutylaluminum chloride (DiIBAlCl) were added via syringe to form a Cr(III)TMHD/DiIBAlCl/Py solution, which was diluted to a total volume of about 8 ml with cyclohexane. 0.25 ml of a 1.1 M (0.28 mmol) TEA solution in heptane and 0.75 ml of the Cr(III)TMHD/DiIBAlCl/Py solution were added to a glass bottle containing 100 ml of cyclohexane and 10 g of butadiene. The glass bottle was placed in a controlled temperature bath at 70°C., at ambient pressure, and agitated for a period of 16 hours. After 16 hours, a small sample of the liquid reaction product mixture was collected and analyzed via gas chromatography. The remaining liquid reaction product mixture was evaporated and the amount of solid product was determined.

The results are summarized below in Table XXVII.

Run 5002

The procedure described in Run 5001 was followed except no excess alkyl aluminum compound was present in the reactor and the catalyst was derived using the procedure described in Run 3001, as follows. 0.21 g (0.601 mmol) of Cracac<sub>3</sub> was combined with 0.12 ml (1.73 mmol) of neat pyrrole and 15 ml of toluene. The resulting solution was stirred under dry nitrogen, at ambient temperature and pressure for 5 minutes. Then, 6.0 ml of a 1.9 M (11.4 mmol) TEA solution in toluene was added. The resulting dark brown reaction mixture was stirred for 5 minutes under dry nitrogen, at ambient temperature and pressure.

Then, 2.0 g of an aluminophosphate support (0.4 P/Al molar ratio, activated at 700°C.) prepared in accordance with U.S. 4,364,855 (1982), herein incorporated by reference, was added and the resulting slurry stirred for a period of approximately 12 hours. The product was collected by filtration, rinsed at least twice with 10 mL aliquots of toluene and pentane, until no color was observed in the filtrate and vacuum dried. The dried product was used as a solid, supported catalyst system.

A 0.28 g catalyst charge was used in the butadiene reaction.

The results are summarized below in Table XXVII.

15

Table XXVII  
Butadiene Reaction

Run	% Butadiene Conversion	Distribution of Products, Weight %		
		to Products	1,5-Cyclooctadiene	Other Liquids Solid
20 5001	97	91.9	0.3	7.8
5002	68	60.8	2.5	36.7

Example VI

In the following Runs, all catalyst systems were prepared in a glove box, under dry nitrogen at ambient temperature and pressure. Transition metal compounds were weighed and combined with three (3) equivalents, (0.062) ml, pyrrole; 2 ml cyclohexane, as a solvent; and 6 ml of a 1.1 M solution of triethylaluminum (TEA) in heptane. The resulting product was shaken for times ranging from 5 minutes to 16 hours.

All runs were carried out in a 1 liter autoclave reactor containing 300 ml cyclohexane. 1.0 ml of the liquid catalyst systems were diluted in cyclohexane and were added to the reactor under a counterflow of ethylene (CP grade). The reactor was

35

sealed and ethylene addition stopped until the reactor temperature reached a reaction temperature of 80°C. The ethylene pressure was increased to a total reactor pressure of 550 psig. Ethylene was fed on demand for a  
5 30 minute run time. If necessary, heat was applied to maintain a reactor temperature of 80°C.

At the end of each run, a sample of the liquid reaction product mixture was taken and analyzed via capillary gas chromatography, on a HP-5880 gas  
10 chromatograph equipped with an FID detector and a 60 meter DB-1 column, with a 0.25 mm ID and a 0.25μ film. The gas chromatograph was ramped from 40°C. to 275°C. at a rate of 10°C./min, with a 20 minute hold time. Cyclohexane was used as an internal standard. The  
15 remaining reaction product mixture was evaporated and the amount of solid product produced was determined.

The results are given in Table XXVIII.



Table XVIII

Run	Metal Compound	Grams, Metal Compound	Catalyst	Grams Catalyst/Charred	Activity, (g product/g catalyst/hr.)	Grams, Total Prod.	Weight Percent Liquid	Weight Percent Solid	Product Distribution, G. = 100 G. = 100 G. = 100
6001	Ni(acac) <sub>3</sub>	0.075	dark brown solution some solids	0.0094	324	1.52	95.4	4.6	4 65 4 7 9
6002	Ni(naph) <sub>3</sub>	0.285	dark brown solution	0.0356	8	0.14	29.5	70.5	74 0 0 4 0 52
6003	Co(acac) <sub>3</sub>	0.075	brown solution, dark solid	0.0094	59	0.28	78.5	21.5	73 13 0 11 1
6004	Mn(acac) <sub>3</sub>	0.073	brown-green solution	0.0091	18	0.08	27.7	72.3	54 0 0 6 0
6005	Mn(acac) <sub>3</sub>	0.102	brown solution	0.0128	12	0.08	23.7	76.3	50 0 0 0 0
6006	Cu(acac) <sub>3</sub>	0.076	dark green solution	0.0095	97	0.46	89.2	10.8	5 0 0 0 0



Table XVIII. Cont.

Run	Metal Compound	Grains, Metal Co- pound	Cata- lyst System Appearance	Grains Catalyst Charged	Activity, (g product/ g catalyst/ hr.)	Grains, Weight total Prod.	Weight Percent		Liquid Product Distribution:		
							Liquid	Solid	Weight Percent	$C_L = \frac{L C_L}{L C_L + C_S} \times 100$	
6007	$\text{MoO}_3(\text{acac})_3$	0.095	green/red solution some solid	0.0119	16	0.10	47.7	52.3	41	0	59
6008	$\text{TiO}(\text{acac})_3$	0.075	-	0.0094	222	1.04	71.2	28.8	11	48	59
6009	$\text{VO}(\text{acac})_3$	0.077	-	0.0096	115	0.56	56.8	43.2	15	50	35
6010	$\text{Zr}(\text{acac})_4$	0.141	-	0.0176	29	0.26	26.8	73.2	0	27	73

The data in Table XXVIII show that other metal compounds can trimerize, oligomerize, and/or polymerize 1-olefins. Of these metal compounds, Ni(acac)<sub>3</sub>, Run 6001, showed the best activity and selectivity toward trimerization.

Example VII

In the following Example, Runs 7001-7005 demonstrate the effect of hydrolyzing the metal alkyl prior to use and the effect of the presence and absence of a pyrrole-containing compound. Runs 7006-7009 compared to Runs 7010-7013 demonstrate the effect of preparation of a catalyst system in an unsaturated hydrocarbon.

Runs 7001-7005

In Runs 7001-7005, the molar ratio of elemental chromium to elemental aluminum to ligand (Cr:Al:L), the catalyst components added to the reactor are 1:30:10. In Runs 7001-7003, the chromium compound was Cr(EH)<sub>3</sub>, and the chromium compound in Runs 7004 and 7005 was Cr(Py)<sub>3</sub>. The aluminum compound was triisobutylaluminum (Al(i-Bu)<sub>3</sub>) and was treated in the following manner. To an approximately ten percent, by weight, solution of triisobutylaluminum in heptane was added 1.0 mole equivalent of distilled water, steadily, but in one batch, while cooling the flask containing the solution with ice water to maintain a temperature of about 10 to about 20°C. The solution was stirred vigorously during and after water addition and continued until no further gas evolution was observed. The ligand was dimethoxyethane (DME).

Runs 7001-7005 were carried out in a 2 liter autoclave reactor. The chromium compound was dissolved in 400-500 ml. anhydrous n-heptane and added to the reactor, under a dry nitrogen purge. Then the appropriate volume of a stirred, treated 0.31 M solution of i-Al(Bu)<sub>3</sub> in heptane, as described above, was added. Then, the appropriate volume of DME was

added, along with 5 ml of nonane (reactor internal standard). The reactor was sealed and brought to a temperature of 80°C. in Run 7001 and 95°C. in Runs 7002-7005 and a pressure of 550 psig with ethylene.

5 Ethylene was fed on demand for a run time of 25 minutes in Run 7001, 30 minutes in Run 7002 and 45 minutes in Runs 7003-7005.

At the end of each run, a sample of the liquid reaction product mixture was taken and analyzed  
10 via capillary gas chromatography, on a HP-5800 gas chromatograph equipped with an FID detector and a 60 meter DB-1 column, with a 0.25 mm ID and a 0.25µ film. The gas chromatograph was ramped from 40°C. to 275°C. at a rate of 10°C./min, with a 20 minute hold time.  
15 The remaining reaction product mixture was evaporated and the amount of solid product produced was determined.

The catalyst systems used in Runs 7006-7013 were prepared according to the following procedures.  
20 Catalyst systems in Runs 7006-7009 were prepared in the presence of toluene, an unsaturated aromatic hydrocarbon. Catalyst systems in Runs 7010-7013 were prepared in the presence of 1-hexene, an unsaturated aliphatic hydrocarbon.

25 Run 7006

3.72 g of  $[\text{Na}(\text{DME})_2][\text{CrCl}(\text{Py})_3\text{DME}]$  was combined with 50 ml toluene. Slowly, 26.4 ml of neat (93%) TEA was added and stirred for 30 minutes. The slurry turned dark brown. Excess solvent was removed  
30 by vacuum, resulting in a dark yellowish/brown oil and solid. About 70 ml cyclohexane was added. The resultant product was filtered and the filtrate was diluted to 260 ml with cyclohexane and 8.0 ml were charged to the reactor. The product contained 1.67 mg  
35 Cr/ml.

Run 7007

0.35 g of chromium(III) ethylhexanoate ( $\text{CrEH}_3$ )

was combined with about 15 ml of toluene, forming a deep green solution. 0.22 ml of 2,5-dimethylpyrrole (2,5-DMP) and 0.20 ml of 1-bromobutane were added. Slowly, 5.7 ml of 1.9 M TEA solution in toluene was added and stirred for 30 minutes to give a greenish, brown solution and a solid. Excess solvent was removed by vacuum and the liquid was extracted into about 15 ml cyclohexane. The resultant product was filtered and the filtrate was diluted to 25 ml with cyclohexane to form a golden colored solution, of which 7.0 ml were charged to the reactor. The product contained 0.014 g  $\text{CrEH}_3/\text{ml}$ .

#### Run 7008

The procedure described in Run 7007 was followed, except 0.22g  $\text{CrEH}_3$  and 0.13 ml of 2,5-DMP were used. Furthermore, 0.10 ml of  $\text{GeCl}_4$  were substituted for the 1-bromobutane. 3.4 ml of 1.9 M TEA solution in toluene was added to give a brown to brown/yellow solution and a precipitate. The final product after filtration and dilution to 25 ml with cyclohexane, was a bright gold-yellow color and contained 0.0088g  $\text{CrEH}_3/\text{ml}$ . 3.0 ml were charged to the reactor.

#### Run 7009

2.070 g of  $\text{CrPy}_3\text{Cl}$  was added to 70 ml toluene and 62 ml of 1.9 M TEA solution in toluene, mixed and filtered. The filtrate volume was reduced to about 20 ml by a dynamic vacuum. The viscous brown solution was filtered again. Then, about 30 ml of pentane was added to the filtrate. After about one day, the solution was vacuum stripped of excess solvent. Then 38.1 g of alumino-phosphate (P/Al molar ratio of 0.9, activation at 700°C.), prepared in accordance with U.S. 4,364,855 were added. The slurry was stirred about 30 hours. The solid was collected by filtration and washed separately with toluene, cyclohexane and pentane. 0.4388 g of the solid catalyst system were charged to the reactor.

Run 7010

0.21 g of  $[\text{Na}(\text{DME})_2][\text{CrCl}(\text{Py})_2\text{DME}]$  was combined with about 15 ml 1-hexane. Slowly, 0.75 ml of neat (93%) TEA was added, forming a brown solution and a sticky-looking precipitate, and stirred for 30 minutes. Excess solvent was removed by vacuum. The residue was extracted into about 15 ml cyclohexane, filtered and the filtrate was diluted to 25 ml with cyclohexane. 8.0 ml (0.067 g) were charged to the reactor.

Run 7011

The procedure described in Run 7010 was followed, except the final catalyst system, in cyclohexane, was aged for about 24 hours prior to use. 8.0 ml (0.067 g) were charged to the reactor.

Run 7012

0.26 g of  $\text{CrEt}_3$  was dissolved in about 15 ml 1-hexane. 0.15 ml of 2,5-DMP and 0.13 ml of 1-bromobutane were added. Slowly, 1.0 ml of neat (93%) TEA was added and stirred for 30 minutes. Excess solvent was removed by vacuum and the liquid was extracted into about 15 ml cyclohexane. The resultant product was filtered and the filtrate was diluted to 25 ml with cyclohexane. 7.0 ml were charged to the reactor.

Run 7013

0.21 g  $[\text{Na}(\text{DME})_2][\text{CrCl}(\text{Py})_2\text{DME}]$  was combined with about 15 ml 1-hexane. Slowly, 1.0 ml of neat (93%) TEA was added, forming a dark brown solution and precipitate, and stirred for about 1 hour. The solution was decanted off and added to 1.5 g of aluminophosphate (P/Al molar ratio of 0.4, activation at 700°C.), prepared in accordance with U.S. 4,364,855, were added.

The supported catalyst system was collected by filtration, washed with 1-hexane and dried under a nitrogen purge. 0.6328 g of the solid catalyst system

were charged to the reactor.

Runs 7006-7013 were carried out in a 1.2 liter autoclave reactor, containing cyclohexane. The heterogeneous, dried, supported catalyst systems (Runs 7009 and 7013) were slurried in cyclohexane to facilitate addition to the polymerization reactor, and were added to the polymerization reactor under a counterflow of ethylene (CP grade). The homogeneous, liquid, unsupported catalyst systems (Runs 7006-7008 and 7010-7012) were diluted in cyclohexane and were added to the polymerization reactor under a counterflow of ethylene (CP grade). The reactor was sealed and ethylene addition stopped until the reactor temperature reached a reaction temperature of 80°C. The ethylene pressure was increased to a total reactor pressure of 550 psig. Ethylene was then fed on demand for a 30 minute run time. At the end of the run, a sample of the liquid reaction product mixture was taken and analyzed via capillary gas chromatography, on a HP-5880 gas chromatograph equipped with an FID detector. The column was a 60 meter DB-1 column with a 0.25 mm ID and a 0.25 $\mu$  film. The gas chromatograph was ramped from 40°C. to 275°C. at a rate of 10°C./min, with a 20 minute hold time. The remaining reaction product mixture was evaporated and the amount of solid product produced was determined.

The results of the reactions are in Table XXIX, below.



Table XXIX

Run	Catalyst (elemental) System	mg Cr Charged	Activity, g product/ g Cr/hr	Grams, Total Products	Weight Percent		Molar Ratios Cr/N/Al/L	Liquid Product Distribution, Weight Percent					
					Liquid	Solid		C <sub>1</sub> = 1-C <sub>2</sub> = C <sub>3</sub> = C <sub>4</sub> = C <sub>5</sub> = C <sub>6</sub> = C <sub>7</sub> =					
7001	Cr(EH) <sub>3</sub> , DME, 1- Al(Bu) <sub>3</sub> ,/ H <sub>2</sub> O	37.6	430	6.8	47	53	1/0/30/10	1	94	<1	4	<1	
7002 (b)	Cr(EH) <sub>3</sub> , DME, 1- Al(Bu) <sub>3</sub> ,/ H <sub>2</sub> O	37.6	3,100	59.1	16	84	1/0/30/10	1	94	1	1	2	
7003	Cr(EH) <sub>3</sub> , DME, 1- Al(Bu) <sub>3</sub> ,/ H <sub>2</sub> O	13.2	4,000	39.7	64	36	1/0/30/10	1	95	<1	2	1	
7004	Cr(Py) <sub>3</sub> , (c) DME, 1- Al(Bu) <sub>3</sub> ,/ H <sub>2</sub> O	13.5	830	8.3	87	13	1/0/30/10	1	89	6	2	7	
7005	Cr(Py) <sub>3</sub> , (c) DME, 1- Al(Bu) <sub>3</sub> ,/ H <sub>2</sub> O	38.7	520	15.0	76	24	1/0/30/10	2	80	4	2	6	
7006	CrCl(Py) <sub>3</sub> , DME, TEA	13.5	7,800	52.6	99.4	0.6	1/3/30/0	<1	82	10	1	7	
7007	Cr(EH) <sub>3</sub> , 25 DHP, TEA, n-BuBr	9.9	25,300	126.8	99.2	0.8	1/3/15/2.5	<1	92	2	<1	5	

Table XXIX Cont.

Run	Catalyst (elemental) System	mg Cr Charged	Activity, g product/ g Cr/hr	Grams, Total Products	Weight Percent		Molar Ratio	Product Distribution, Weight Percent		
					Liquid	Solid		Cr/N/Al/L	Cr	N
7008	Cr(EH) <sub>3</sub> , 25 DMP, TEA, GeCl <sub>4</sub>	2.7	66,403	87.7	99.9	0.1	1/3/15/2.5	<1	98	<1
7009	CrCl(Py) <sub>3</sub> , DME, 0.9 P/Al	0.397g Catalyst	69 <sup>d</sup>	14.0	97.1	2.9	1/3/30/0	<1	87	7
7010	CrCl(Py) <sub>3</sub> , DME, TEA	6	5,200	16.3	96.3	3.7	1/3/15/0	16	55	2
7011	CrCl(Py) <sub>3</sub> , DME, TEA	6	5,070	15.9	96.2	3.8	1/3/15/0	15	55	2
7012	Cr(EH) <sub>3</sub> , 2.5 DMP, TEA, n-BuBr	7.4	10,200	38.9	96.7	3.3	1/3/15/0	3	74	5
7013	CrCl(Py) <sub>3</sub> , DME, TEA, 0.4 P/Al	0.6320g Catalyst	34 <sup>d</sup>	19.0	56.8	43.2	1/3/15/2.5	9	45	3

a) N is nitrogen containing compound, i.e., pyrrole-containing compound; L is ligand.

b) Reactor plugged with solids.

c) CrCl(Py)<sub>3</sub> is equivalent to Cr(Py)<sub>3</sub>, both of which are [Na(DME)<sub>2</sub>] [CrCl(Py)<sub>3</sub>·DME].

d) Activity is in units of g product/g catalyst/hr.



The data in Table XXIX shows that the presence of water (Runs 7001-7005) is detrimental to the formation of liquids, such as for example, 1-hexene. In fact, water in the reactor results in high solids formation.

Runs 7006-7013 show that catalyst systems prepared in the presence of any unsaturated hydrocarbon are effective toward trimerization. However, comparison of Runs 7006-7009, prepared in toluene, with Runs 7010-7013, prepared in 1-hexene, show that an unsaturated aromatic hydrocarbon is the preferred catalyst system preparation medium.

#### Example VIII

The following Example, Runs 8001-8017, demonstrates the effect of varying the pyrrole compound, halogen, and metal additive used.

Catalyst systems used in Runs 8001-8017 were all prepared in the same general procedure. In a typical preparation, chromium(III) 2-ethylhexanoate was dissolved in toluene. Next, 3 equivalents of 2,5-dimethylpyrrole (or hydrogen pyrrolide for Runs 8014-8017) was added to the solution. The desired amount of halide additive (2 to 3 molar equivalents) was then added, followed by 15 molar equivalents of triethylaluminum (TEA). The reaction mixture was stirred for 5-10 minutes and toluene was removed under vacuum. The liquid residue was diluted to a total volume of 10 ml with cyclohexane and an aliquot was charged to the reactor as the catalyst system.

The trimerization reaction runs were carried out in a 2-liter autoclave polymerization reactor containing 1.2 liters of 85% cyclohexane as the reactor diluent. Catalyst system was charged to the reactor followed by addition of cyclohexane. The reactor temperature was brought to 80°C. at which point ethylene was introduced. The pressure was maintained at 550 psig with ethylene fed on demand. Each reaction

was run for 30 minutes before shutting off ethylene. Samples were taken at the end of the run and analyzed by gas chromatography, as described in other examples.

The results of the Runs and analyses are given in Table XXX.

5

Table XXV

Run	Additive	mg Cr Charged	Molar Ratio Cr/Pv/TBA/Add	Activity, <sup>a</sup> g liquid/g Gr/hour	Total Prod. Grams	Wt. % Liquid	Wt. % Solid	Liquid Product Distribution, Weight Percent		
								1-Cr	Cr	Cr
8001	None	13.7	1/3/15/0	4700	33.7	95	5	30	43	6 5 13
8002	DEAC	14.2	1/3/15/3	16800	121.2	99	1	<1	86	3 1 8
8003	DEAB	6.6	1/3/15/3	1800	61.5	98	2	<1	99	2 <1 4
8004	DEAL-I	13.7	1/3/15/3	630	5.0	86	14	4	72	8 2 12
8005	n-BuCl	6.8	1/3/15/3	6300	21.9	98	2	18	52	7 3 16
8006	n-BuBr	6.9	1/3/15/2.5	27500	95.0	>99	<1	<1	91	2 <1 5
8007	n-BuBr	9.9	1/3/15/2.5	25300	126.8	>99	<1	<1	92	2 <1 5
8008	n-BuI	6.1	1/3/15/3	2020	7.2	85	15	4	71	7 2 14
8009	Me <sub>3</sub> SiCl	14.6	1/3/15/3	3600	26.9	97	3	16	57	6 4 14
8010	Me <sub>3</sub> SiBr	6.6	1/3/15/3	14000	46.6	>99	<1	<1	86	4 <1 8
8011	GeCl <sub>4</sub>	6.6	1/3/15/2	55000	181.7	>99	<1	<1	96	<1 <1 3
8012	GeCl <sub>4</sub>	2.7	1/3/15/2	66400	87.7	>99	<1	<1	98	<1 <1 <1
8013	SnCl <sub>4</sub>	6.9	1/3/15/2	40600	140.4	>99	<1	<1	96	<1 <1 2
8014	DEAC	10.8	1/3/15/2.5	6900	38.5	96	4	<1	87	4 2 5
8015	DEAB	10.8	1/3/15/2.5	2600	14.3	97	3	<1	89	3 2 4
8016	DEAL-I	10.8	1/3/15/2.5	70	0.4	44	56	19	60	6 3 4
8017	GeCl <sub>4</sub>	10.8	1/3/15/2.5	3300	19.0	94	6	<1	95	2 1 2

<sup>a</sup>) Based on grams liquid product only.

The data in Table XXX show that the selectivity towards 1-hexene increases in the order  $I < Cl < Br$ . The bromine-containing additives consistently have the highest selectivity for the formation of 1-hexene compared to the corresponding chloride or iodide additive. The increased production of 1-hexene also means that less byproducts ( $C_4=$ ,  $C_8=$ , and  $C_{10}=$ ) are being formed. The ratio of 1-hexene to internal hexenes also tends to increase in the order  $I < Cl < Br$ . Thus, the use of halides leads not only to more product, but a cleaner trimer product as well. The activity of the catalyst system increases in the order  $I < Cl, Br$ . However, the activity between Br and Cl analogues appear to be unpredictable. For some additives ( $SnX_4$ , and  $AlX_3$ ,  $SiX_4$ ) the Br is more active.

The data in Table XXX also show that the trend in selectivity to 1-hexene and activity can be extended to catalysts containing other pyrroles, as shown in Runs 8014-8017.

Overall, the best combination of activity and selectivity is obtained using  $GeCl_4$  or  $SnCl_4$  as the halide additives. However, it has been shown that the selectivity towards 1-hexene is also affected by the ratio of halide additive to triethylaluminum, making it possible to obtain high selectivity from other halide additives.

#### Example IX

In the following Example, Runs 9001-9004 demonstrate that excess unsaturated aromatic hydrocarbon can be detrimental to trimerization and/or oligomerization. Thus, when a catalyst system is prepared in the presence of an aromatic hydrocarbon, such as, for example, toluene, removal of excess aromatic hydrocarbon is preferred. The resulting liquid is then extracted or dissolved into a desired solvent, such as, for example cyclohexane or heptane. While not wishing to be bound by theory, it is believed

that an aromatic hydrocarbon can compete with a monomer to be trimerized and/or oligomerized, such as, for example, ethylene, for an active site of the catalyst system. Thus, it is believed that this competition can inhibit catalyst system activity.

The catalyst system used in Runs 9001-9004 was prepared using 1.35 g of chromium(III) 2-ethylhexanoate dissolved in toluene. Next, 0.86 mL (3.2 molar equivalents) of 2,5-dimethylpyrrole was added to the solution. Then 0.90 mL (3.2 molar equivalents) of n-butylbromide was added, followed by 7.60 mL (21 molar equivalents) of 93% triethylaluminum. The mixture was stirred for 5-10 minutes and toluene was removed under vacuum. The liquid residue was dissolved into 30 mL of cyclohexane, filtered, and then diluted to a total volume of 50 mL with additional cyclohexane. Four (4) mL of this solution was charged along with the desired amount of anhydrous, degassed toluene (0, 5, 10 or 15 mL) to the reactor.

The trimerization reaction runs were carried out in a 2-liter autoclave polymerization reactor containing 1.2 liters of 85% cyclohexane as the reactor diluent. Catalyst system was charged to the reactor followed by addition of cyclohexane. The reactor temperature was brought to 80°C. at which point ethylene was introduced. The pressure was maintained at 550 psig with ethylene fed on demand. Each reaction was run for 30 minutes before shutting off ethylene. The total amount of ethylene consumed, i.e., fed, was measured.

The results of Runs 9001-9004 are given in Table XXXI.

**Table XXXI**  
**Effect of Aromatic Hydrocarbons**  
**on Catalyst System Activity**

Run	Toluene Added, ml	Toluene Added, Volume % <sup>(a)</sup>	Ethylene Consumed After 30 mins <sup>(b)</sup> , g
9001	0	0.00	184
9002	5	0.42	160
9003	10	0.83	127
9004	15	1.25	109

<sup>a)</sup> Based on total value of reactor diluent.

<sup>b)</sup> Not adjusted for solubility of ethylene in cyclohexane.

15

The data in Table XXXI show that the presence of an aromatic hydrocarbon, i.e., toluene, can result in a significant decrease in the activity of the catalyst system, as measured by ethylene consumption.

20

This decrease is proportional to the amount of aromatic hydrocarbon added to the reactor.

The claims defining the invention are as follows:

1. A process to prepare a catalyst system comprising combining a metal source, a pyrrole-containing compound and a metal alkyl in a mutual solvent without a preliminary reaction step between the metal source and the pyrrole-containing compound in the presence of an electron donor solvent.
2. A process according to claim 1, in which an unsaturated hydrocarbon is also combined, said unsaturated hydrocarbon optionally providing the mutual solvent.
3. A process according to claim 2, wherein said unsaturated hydrocarbon is an aromatic or aliphatic hydrocarbon having less than about 70 carbon atoms per molecule.
4. A process according to claim 3, wherein said unsaturated hydrocarbon is an aromatic hydrocarbon having less than about 20 carbon atoms per molecule.
5. A process according to claim 4, wherein said aromatic unsaturated hydrocarbon is toluene, benzene, xylene, mesitylene, or hexamethylbenzene.
6. A process according to any one of claims 2-5, which includes stripping excess unsaturated aromatic hydrocarbon from the resulting catalyst system.
7. A process according to claim 3, wherein said unsaturated hydrocarbon is ethylene.
8. A process according to any one of the preceding claims, wherein said metal source is a chromium, nickel, cobalt, iron, molybdenum, or copper compound.
9. A process according to claim 8, wherein the metal source is a chromium compound.
10. A process according to any one of the preceding claims, wherein said pyrrole-containing compound is pyrrole or 2,5-dimethylpyrrolide.
11. A process according to any one of the preceding claims, wherein the metal of the metal alkyl is aluminum, lithium, magnesium, or zinc.
12. A process according to claim 11, wherein said metal alkyl is an aluminum alkyl.
13. A process according to claim 12, wherein said aluminum alkyl is a trialkyl aluminum compound, such as



triethyl aluminum.

14. A process according to any one of the preceding claims, in which a support is incorporated into the catalyst system.

15. A process according to claim 14, wherein said support is an inorganic oxide.

16. A process according to claim 15, wherein said inorganic oxide is silica, silica-alumina, alumina, fluorided alumina, silylated alumina, thorina, aluminophosphate, aluminum phosphate, phosphated silica, phosphated alumina, silica-titania, coprecipitated silica/titania, fluorided/silylated alumina, or a mixture thereof.

17. A process according to any one of the preceding claims, which includes adding a halide source.

18. A process according to claim 17, wherein said halide is a chloride or bromide or a mixture thereof.

19. A process according to claim 17 or 18, wherein said halide is provided by a compound having a formula of  $R_mX_n$ , wherein R is an organic or inorganic radical, X is a halide, and the sum of m plus n is any number greater than 0.

20. A process according to claim 19, wherein R is aluminum, silica, germanium, hydrogen, boron, lithium, tin, gallium, indium, lead, or a mixture thereof.

21. A process according to claim 20, wherein R is tin, germanium, or a mixture thereof.

22. A process according to any one of the preceding claims, in which the resulting catalyst system has a relative ratio of:

- (a) about 1 mole of the metal of the metal source;
- (b) about 1 to about 15 moles of the pyrrole-containing compound;
- (c) about 5 to about 40 moles of the metal alkyl; and, if present,
- (d) about 1 to about 30 moles of the halide.

23. A process according to any one of the preceding claims, which is carried out in the absence of oxygen and water.

24. A process according to any one of the preceding claims, wherein the metal source and the pyrrole-containing compound are combined prior to the addition of the metal

alkyl.

25. A process to prepare a catalyst system comprising reacting a mixture of:

- (a) a metal salt;
- (b) pyrrole or a substituted pyrrole; and
- (c) an electron pair donor solvent and reacting the resulting reaction product with a metal alkyl; and, if desired, reacting the resulting reaction product with an unsaturated hydrocarbon.

26. A process according to claim 25, wherein said metal salt is a chromium salt.

27. A process to prepare a catalyst system comprising reacting a mixture of:

- (a) a salt of a metal other than chromium;
- (b) a metal amide; and
- (c) an electron pair donor solvent and reacting the resulting reaction product with a metal alkyl; and if desired, reacting the resulting reaction product with an unsaturated hydrocarbon.

28. A process according to claim 27, wherein said metal salt is a nickel, cobalt, iron, molybdenum, or copper salt.

29. A process to prepare a catalyst system comprising reacting a mixture of:

- (a) a metal salt;
- (b) a metal amide; and
- (c) an electron pair donor solvent and reacting the resulting reaction product with a metal alkyl; and reacting the resulting reaction product with an unsaturated aliphatic hydrocarbon comprising less than 20 carbon atoms per molecule.

30. A process according to claim 29, wherein said aliphatic hydrocarbon is ethylene.

31. A process according to any one of the preceding claims, which comprises admixing the catalyst system prepared as a cocatalyst system with a polymerization catalyst system.

32. A process according to claim 31, in which the polymerization catalyst system comprises a chromium-, titanium-, zirconium- and/or vanadium-containing catalyst.



33. A process to trimerize, oligomerize or polymerize an olefin compound which comprises carrying out said trimerization, oligomerization or polymerization in the presence of a catalyst system or catalyst/cocatalyst system prepared by a process according to any one of the preceding claims.

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34. A process according to claim 33, wherein said olefin compound has from about 2 to about 30 carbon atoms per molecule and at least 1 olefinic double bond.

35. A process according to claim 34, wherein said olefin compound is ethylene, 1-butene, 1-hexene, 1,3-butadiene, or a mixture thereof.

36. A process according to any one of claims 33-35, in which an unsaturated hydrocarbon is combined to prepare the catalyst system but is first introduced during the trimerization, oligomerization or polymerization process.

37. A process according to claim 36, in which the unsaturated hydrocarbon used to prepare the catalyst system is an unsaturated aliphatic hydrocarbon also acting as the olefin compound which is trimerized, oligomerized or polymerized.

38. A process for preparing a polymerization system or catalyst/cocatalyst system substantially as herein described with reference to any one of the examples.

39. A polymerization system or catalyst/cocatalyst system when prepared by a process according to any one of claims 1-32 and 38.

40. A process to trimerize, oligomerize or polymerize an olefin compound substantially as herein described with reference to any one of the examples.

41. A trimer, oligomer or polymer when prepared by a process according to any one of claims 33-37 and 40.

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# ABSTRACT

Improvements or modifications of earlier process for preparing chromium-containing compounds, such as, for example, chromium pyrrolides, by forming a mixture of a chromium salt, a metal amide, particularly a pyrrolide, and an electron pair donor solvent, such as, for example, an ether, and reaction with an unsaturated hydrocarbon are disclosed, including use of pyrrole or derivatives thereof as the pyrrolide and an aliphatic as the unsaturated hydrocarbon. A new process for preparing a catalyst system comprises combining a metal source, a pyrrole-containing compound and a metal alkyl without a preliminary reaction step between the metal source and the pyrrole-containing compound in the presence of an electron donor solvent. These catalyst systems and chromium-containing compounds either unsupported or supported on an inorganic oxide support, if desired functioning as a cocatalyst in combination with another polymerization catalyst, such as containing chromium or titanium, can be used to trimerize, oligomerize, and/or polymerize olefins.

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